TABLE 5.3 SUMMARY OF ANALYTICAL CONDITIONS FOR ANALYSIS OF TRACE METALS IN SEDIMENTS

Element	Instrument	Instrument Conditions	Detection Limit	Procedural Blank
			(ug/g dry weight)	
Ba	ICAP	493.41 nm 1st order; FP 2.3 Kw Observation height 20 mm Nebulizer flow 2.5 mL/min	0.4	1.8
Ba	XRF	Tungsten tube 70 Kv, 20 ma Gadolinium secondary source Counting time 3000 sec	50	0
Cd	ZGFAA	Pyrolytic tube; Ammonium phosphate matrix 10 µL; 228.8 nm; slit 0.7 nm Hollow cathode lamp 4 ma Gas 50 mL/min; 80°C and 140°C dry; 250°C and 500°C ash 1500°C atomization; 2600°C clean	0.04	0.1
Cr	ICAP	266.72 nm 3rd order; FP 1.2 Kw Observation height 20 mm Nebulizer flow 2.5 mL/min	1.2	9.1
Cu	ICAP	324.75 nm 2nd order; FP 1.2 Kw Observation height 20 mm Nebulizer flow 2.5 mL/min	0.9	0.9
Cu	XRF	Tungsten tube 40 Kv, 20 ma Zirconium secondary source Counting time 3000 sec	0.5	0
Pb	XRF	Tungsten tube 40 Kv, 20 ma Zirconium secondary source Counting time 3000 sec	0.5	0
Pb	ZGFAA	Pyrolytic tube; Ammonium phosphate matrix 10 µL; 283.3 nm; slit 0.7 nm Electrodeless discharge lamp 10 W Gas 50 mL/min; 80°C and 140°C dry; 250°C and 800°C ash 2100°C atomization; 2600°C clean	0.3	1.5
V	ICAP	292.40 nm 2nd order; FP 1.2 Kw Observation height 20 mm Nebulizer flow 2.5 mL/min	0.4	1.4
Zn	ICAP	213.86 nm 3rd order; FP 1.2 Kw Observation height 20 mm Nebulizer flow 2.5 mL/min	6.0	4.8
Zn	XRF	Tungsten tube 40 Kv, 20 ma Zirconium secondary source Counting time 3000 sec	0.5	0

TABLE 5.4 SUMMARY OF ANALYTICAL CONDITIONS FOR ANALYSIS OF TRACE METALS IN TISSUES

ELEMENT	INSTRUMENT	INSTRUMENT CONDITIONS	Detection Limit	Procedural Blank
			(ug/g dry weight)	
Ba	ICAP	493.41 nm 1st order; FP 2.3 Kw Observation height 20 mm Nebulizer flow 2.5 mL/min	0.01	0.04
Cd	ZGFAA	Pyrolytic tube; Ammonium phosphate matrix 10 µL; 228.8 nm; slit 0.7 nm Hollow cathode lamp 4 ma Gas 200 ml/min 80°C and 140°C dry; 250°C and 600°C ash 1500°C atomization; 2600°C clean	0.04	0.6
Cr	ZGFAA	Pyrolytic tube; 357.9 nm; slit 0.7 nm Hollow cathode lamp 25 ma Gas flow zero 80°C and 140°C dry; 250°C and 1300°C ash; 2300°C atomization; 2600°C clean	0.04	0.7
Cu	ICAP	324.75 nm 2nd order; FP 1.2 Kw Observation height 20 mm Nebulizer flow 2.5 mL/min	0.5	0.5
Pb	ZGFAA	Pyrolytic tube; Ammonium phosphate matrix 10 µL; 283.3 nm; slit 0.7 nm Electrodeless discharge lamp 10 W Gas flow zero 80°C and 140°C dry; 250°C and 750°C ash; 2000°C atomization; 2600°C clean	0.06	0.5
V	ICAP	292.40 nm 2nd order; FP 1.2 Kw Observation height 20 mm Nebulizer flow 2.5 mL/min	1.2	1.1
Zn	ICAP	213.86 nm 3rd order; FP 1.2 Kw Observation height 20 mm Nebulizer flow 2.5 mL/min	0.1	1.0

Two digestion procedures were used to totally dissolve the sediment. For ICAP analysis, 0.25 g of dry ground sediment was combined with 2 mL of aqua regia and 6 mL of hydrofluoric acid in a Teflon vial. The vial was sealed with a screw cap and heated on a hot plate at 80-90°C for 2 h. The vial lid was removed and the solution was evaporated to near-dryness to remove the hydrofluoric acid. The resulting residue was dissolved in 0.4N nitric acid.

For analysis by ZGFAA, 0.1 g of sediment was combined with 7 mL of hydrochloric acid in a Teflon vial. The sealed vial was heated in an 80-90°C water bath for 1 h. After cooling, 0.5 mL of hydrofluoric acid was added to the vial, which was again heated in the water bath for 1 h. When cool, the digestate was transferred to a polystyrene container and diluted to 50 mL with double deionized water.

Approximately 10 percent of the sediments were analyzed by XRF as a cross-check to verify the ICAP results. Some sediment samples were additionally analyzed for copper, lead, and zinc by XRF. Sediment samples were prepared for XRF by pressing 0.5 g of powdered sediment into a 25-mm-diameter pellet. The analysis was performed on a Kevex spectrometer using a zirconium secondary target for excitation of copper, lead, and zinc. Data reduction methods are described by Nielson (1977).

5.3.2 Methods for Tissues

Biota samples were received frozen and were stored at -20°C until analysis. In preparation for analysis, the organisms were thawed, cleaned, using Teflon forceps, of foreign matter, and rinsed with double deionized water. Using Teflon forceps and a titanium knife, individual bivalves were removed from their shells. A pool of 5 to 10 individuals of the same species was placed in an acid-cleaned, preweighed plastic jar, the wet weight recorded, and the tissue freeze-dried to a constant weight. After recording the dry weight, the tissue was ground to a powder in an all-plastic Spex 8000 ball mill.

Tissues were digested by combining 0.25 g of dry, powdered tissue with 5 mL of nitric acid in a screw-cap Teflon vial, and heating this for 8 h at 130°C. After cooling, 1 mL of hydrofluoric acid was added, the vial sealed, and the mixture digested for 2 h. After evaporation to near-dryness, the residue was diluted with deionized water to 25 mL, followed by acidification with 25 μL nitric acid. Analysis was performed using ZGFAA.

5.3.3 Quality Control Methods

Quality control relating to metals analysis of sediment and tissues included analysis of reagent blanks, procedural blanks, and standard reference materials (SRMs).

Prior to analysis of environmental samples, labware blanks and reagent blanks were analyzed in triplicate for each lot to determine that the blanks were acceptable. Procedural blanks were run through the entire analytical process to check for contamination, to establish a reagent blank that is subtracted from the sample results, and to determine detection limits. Five procedural blanks were run with every batch of samples analyzed. The detection limit for each element in both sediment and tissue was defined as 2 times the standard deviation of the background signal for the procedural blanks.

SRMs (sediment MESS-1 and oyster tissue NBS-SRM 1566) were analyzed with each batch of samples to verify accuracy and precision of the analytical results. At least 1 SRM was analyzed for every 20 environmental samples.

The precision of each analytical instrument for each metal was detemined by analysis of five replicates of a certified homogeneous sediment and tissue SRM. Field samples and SRMs were analyzed for barium, copper, lead, and zinc by two different techniques to verify that the sediment digestion procedures totally dissolved the sediments. The XRF technique determined total metals without sediment digestion.

The method of standard additions was used to evaluate matrix effects for both ICAP and ZGFAA. Ammonium phosphate was used as a matrix modifier in the ZGFAA analysis of cadmium and lead to improve the analytical signal and precision. The Zeeman effect background correction system was used for all ZGFAA analyses.

The results of the quality control procedures are presented in Appendix B and discussed in Section 6.3.

5.4 HYDROCARBON CHEMISTRY

In Year-1, the general analytical strategy for hydrocarbon analysis consisted of two levels (see Figure 5.7). In the first level, which was used as a general screening technique, sample replicates were extracted and analyzed by UV/F to measure approximate concentrations of aromatic hydrocarbons. Sample replicates of additional interest were individually carried through to the second level, consisting of GC-FID and computer-assisted GC/MS analysis for determination of individual saturated and aromatic hydrocarbons, respectively.

In subsequent years of the program, the first level UV/F scan was eliminated from the sediment analysis scheme because of high background fluorescence and the limited potential use of this measurement in Beaufort Sea monitoring studies. A complete hydrocarbon analysis by GC-FID and GC/MS was performed on all pooled sediment replicates in Year-2 and Year-3 (discussed in Section 5.1.1).

5.4.1 Sediment Preparation Methods

Extraction and clean-up procedures followed Brown et al. (1979) and Boehm et al. (1982a), and are outlined in Figure 5.7. For analyses of bulk sediments, approximately 100 to 150 g of wet sediment (from individual or composited replicates) were thawed at room temperature and weighed into a 250-mL Teflon jar. In Year-2, sediments from three stations were also separated into the fine (silt + clay) fraction by wet sieving through a 63-μm stainless steel sieve, followed by centrifugation.

Bulk sediments were dried by extracting three times with 50 mL of methanol. The mud fractions were extracted in the centrifuge bottle with methanol/dichloromethane and the aqueous supernatant was used for back extraction of the methanolic extract. The following procedures were employed for both the bulk sediments and the mud fractions.

Five micrograms of each of the two quantification internal standards (androstane for saturated hydrocarbons and o-terphenyl for aromatic hydrocarbons) were added to the sediments. The dried sediments were extracted three times with 100-mL aliquots of dichloromethane:methanol (9:1) by agitating on a platform shaker 4 h for each extraction. All solvent extracts were transferred into a 1-L separatory funnel containing 100 mL Milli-Q water and 10 g sodium chloride. The dichloromethane layer was drawn off and the aqueous methanol phase extracted three times with 50-mL aliquots of dichloromethane. The combined dichloromethane extracts were dried over sodium sulfate, concentrated to 1 mL by rotary or Kuderna-Danish evaporation, and displaced with hexane. Single aliquots of extracts were weighed on a Cahn Model-25 electrobalance to determine total extractable organics.

The extracts were fractionated by silica gel/alumina column chromatography into saturated (f1) and unsaturated/aromatic (f2) fractions. Column chromatography was performed using a 5% deactivated silica/1% deactivated alumina/activated copper (11:1:2 g) 1-cm i.d. chromatography column that was wet packed in dichloromethane and prepared by eluting with 30 mL each of dichloromethane and hexane. The sample extract, which was less than 50 mg extract weight in 0.5 mL hexane, was charged to the column and eluted with 18 mL hexane to isolate the saturated (f1) hydrocarbons, followed by 21 mL hexane:dichloromethane (1:1) to isolate the unsaturated/aromatic (f2) hydrocarbons. The f1 and f2 fractions were analyzed by GC-FID and GC/MS, respectively.

5.4.2 Tissue Preparation Methods

Approximately 3 to 15 g wet weight tissue were extracted and cleaned up according to the procedures of Boehm et al. (1982b). Bivalve tissues were removed from the shells with solvent-rinsed utensils and a wet weight was obtained on a top-loading balance. Whole amphipods and shucked bivalves were digested overnight with 5N aqueous potassium hydroxide and the digestate was extracted three times with ethyl ether. The extracts were combined, dried over sodium sulfate, and concentrated to 0.5 mL by rotary or Kuderna-Danish (K-D) evaporation. Polar and biogenic compounds that interfere with UV/F analysis were removed from the extracts by alumina (6.5 g of 7.5% water-deactivated alumina) column chromatography. The column was eluted with 25 mL hexane/dichloromethane (9:1) to isolate the saturated and unsaturated/aromatic compounds. The fraction was concentrated and transferred into hexane for UV/F analysis.

Following the UV/F analysis, individual or pooled extracts obtained from individual replicates were concentrated by nitrogen evaporation and displaced with hexane. Total extracts were separated into f1 and f2 fractions according to procedures described above for sediments. The f1 saturated and f2 unsaturated/aromatic fractions were analyzed by GC-FID and GC/MS, respectively.

5.4.3 Analytical Methods

5.4.3.1 UV/F

The technique of synchronously scanning the corrected excitation and emission monochrometers of a scanning spectrofluorometer was based on the methods of Wakeham (1977), Gordon et al. (1976), John and Soutar (1976), Boehm et al. (1982c), and Boehm and Fiest (1982). UV/F was used to analyze sediment extracts from Year-1 and all tissue extracts.

The sample extract (or a dilution thereof) was dissolved in hexane for analysis by UV/F. The intensity of the fluorescence emission was measured from 250-500 nm, while synchronously scanning the excitation monochrometer at a wavelength of 25 nm shorter than the wavelength of the emission monochrometer. This technique measures the 2- to 5-ring aromatic hydrocarbons (Lloyd, 1971). The intensities of the fluorescence spectra were measured at 312, 355, and 425 nm, which correspond to approximate peak maxima of the 2-, 3-, and 4- plus 5-ring aromatics present in the samples and in the Prudhoe Bay crude oil reference standard.

A dilution series of the hexane/crude oil was used to calibrate the method daily. Calibration curves, based on the analysis of Pruhoe Bay crude oil standard, were used to quantify

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sample extracts. UV/F data are presented in μg Prudhoe Bay crude oil equivalents per g dry sediment weight or per g wet tissue weight.

5.4.3.2 GC-FID

GC-FID analysis was used to identify and quantify the saturated petroleum hydrocarbon compounds present in the samples. The concentrations of specific compounds were also used to calculate indicator ratios for use in testing the null hypotheses.

Each extract fraction was analyzed by fused silica capillary gas chromatography on either a Hewlett-Packard 5880A or a Shimadzu Model GC9A gas chromatograph equipped with a splitless injection port, a flame ionization detector (FID), and a Shimadzu C-R3A data system. Fused silica capillary columns (0.25 mm x 30 m; J&W Scientific), coated with bonded DB-5 stationary phase, were used to analyze the f1 saturated hydrocarbon fraction from column chromatography. Instrumental conditions are listed in Table 5.5

On the Shimadzu C-R3A, hydrocarbon concentrations were calculated using internal standards. The computerized data system automatically identified compounds by comparing retention indices of peaks in the samples to retention indices of known compounds in a standard mixture. Concentrations were calculated by comparing the integrated areas of peaks with the area of the appropriate internal standard (androstane or cholestane) and applying a determined response factor. The total concentration of saturated hydrocarbons was determined by integrating the unresolved complex mixture (UCM) area, adding to it the total resolved integrated area, and calculating a concentration using internal standards. The concentrations of n-alkanes and isoprenoids were determined in μg/g on a dry-weight basis for sediments and on a wet-weight basis for tissues.

5.4.3.3 GC/MS

The f2 aromatic fraction was analyzed on a Finnigan 4530 GC/MS equipped with a 0.25-mm x 30-m DB-5 fused silica capillary column (J&W Scientific) that was threaded directly into the ion source. Instrumental conditions are listed in Table 5.6. Selected ion searches were used to obtain ion chromatograms for aromatic compounds with known retention indices. Concentrations of the identified compounds were determined by measuring peak areas (ion currents) of the appropriate peaks in the selected ion chromatograms and relating them to the peaks of the internal standard. Relative response factors for each component were calculated from analyses of analytical standards, if available, or by extrapolation. Compounds detected by GC/MS analyses for this study are listed in Table 5.2.

TABLE 5.5 FUSED SILICA CAPILLARY GAS CHROMATOGRAPHY/FLAME IONIZATION DETECTION ANALYTICAL CONDITIONS

Instrument:	Shimadzu GC-9A gas chromatograph Shimadzu C-R3A integrator/data processor
Features:	Split/splitless capillary inlet system Microprocessor-controlled functions Automatic data reduction/floppy disk data storage
Inlet:	Splitless
Detector:	Flame ionization
Column (f_1):	0.25 mm ID x 30 m SE30 fused silica (J & W Scientific) DB1 fused silica (J & W Scientific)
Gases:	
Carrier:	Helium, 2 mL/min
Make-up:	Helium, 30 mL/min
Detector:	Air, 300 mL/min Hydrogen, 30 mL.min
Temperatures:	
Injection port:	250°C
Detector:	300°C
Column oven:	40-290°C at 3°C/min
Daily calibration:	Alkane mixture
Quantification:	Internal standard (f_1 androstane; cholestane)

TABLE 5.6 GAS CHROMATOGRAPHY/MASS SPECTROMETRY INSTRUMENTAL CONDITIONS

Instrument:	Finnegan 4530 gas chromatograph/mass spectrometer
Features:	Data General Nova-4 system with Incos data system Finnegan MAT 9610
Inlet:	Splitless
Detector:	Quadrupole mass spectrometer
Scan rate:	450 amu/sec (45-450 amu)
Ionization voltage:	70 eV
Column:	0.25 mm ID x 30 m SE54 fused silica (J & W Scientific)
Interface:	Direct insertion of column into source
Carrier gas:	Helium, 2 mL/min
Temperatures:	
Injection port:	270°C
Separator oven	280°C
Source:	250°C
GC oven:	40-290°C at 10°C/min
Daily calibration:	FC43, DFTPP, and aromatic mixture
Quantification:	Internal standard (o-terphenyl) response factors

5.4.4 Quality Control Methods

The geochemistry quality assurance program is part of the formal laboratory-wide quality assurance program instituted at Battelle. The requirements of this program consisted of an initial demonstration of laboratory capability and analysis of spiked samples as an ongoing check on performance. Specific measures, taken before iniciation of this study and during the course of the program, included

- A rigorous on-the-job training program that included a demonstration of training through analysis of triplicate samples and blanks;
- Adherence to strict sample transfer and custody procedures;
- Laboratory and data book audits;
- Documented calibration of UV/F, GC-FID, and GC/MS instruments on a daily basis; and
- An ongoing analytical quality control program.

Program-specific components of the analytical quality control program additionally included demonstration of laboratory capability through analysis of interim reference materials (sediment and mussel tissue). During Year-1 of the study, reference sediment from the National Oceanic and Atmospheric Administration/National Analytical Facility (NOAA/NAF) was analyzed. In Year-2, sediment and mussel tissue, provided by NOAA's National Marine Fisheries (NMF) Laboratory in Seattle, was analyzed. For the Year-3 program, the NOAA reference sediment was not received in time to include the data in this report. Canadian Test Sediment HS-2, from the Marine Analytical Research Laboratory in Halifax, Nova Scotia, was, however, analyzed as reference material in Year-3.

The ongoing analytical quality control program also included analysis of method blanks with every batch of sediment or tissue analyzed, analysis of spiked blanks for the determination of recoveries of selected compounds, and matrix spikes or re-extraction of samples to monitor the efficiency of extraction.

The results of the analytical quality control program are presented in Appendix B.

5.5 METHODS FOR AUXILIARY MEASUREMENTS AND PARAMETERS

In addition to the trace metal and hydrocarbon determinations made for this program, hydrographic measurements, sediment grain size, and total organic carbon were included to aid in the interpretation of the geochemical data.

5.5.1 Hydrography

Hydrographic measurements were made only during the first field program (Year-1). The hydrographic data were collected in support of the analytical program and were not used to characterize water masses. These data included temperature, salinity, and dissolved oxygen of the water column at each of the 27 stations occupied. Where possible, these measurements were recorded at three depths in the water column, although at some extremely shallow stations, only surface and bottom measurements could be recorded. Because the hydrographic data proved to be of little value to the overall objectives of the monitoring program, the hydrography was not performed on subsequent surveys.

Primary hydrographic measurements were taken with a Hydrolab Series 4041 in situ instrument with digital readout. The Hydrolab consists of a probe (Sonde) attached to an electronics module by an electro-mechanical cable. The probe contains sensors of temperature, conductivity, and dissolved oxygen. The precision of the instrument is listed below by parameter:

Parameter	Precision
Temperature	± 0.05°C
Salinity	± 0.05°/oo
Dissolved Oxygen	± 0.05 ppm

Calibration of the temperature probe at each station was performed with a bucket thermometer that complied with all requirements of the National Bureau of Standards (NBS). At each station, the conductivity probe was calibrated with a secondary seawater standard of known salinity. The secondary standard was analyzed on a Beckman salinometer both before and after the cruise. The dissolved oxygen probe was calibrated at each station by using a wet air calibration that relies on the known solubility of oxygen in distilled water at any given temperature. Discrete water samples were also collected by Niskin bottle and preserved for oxygen analysis by the Winkler method. This analysis was originally intended to provide a quality control check on the dissolved oxygen probe, [illegible] became the primary measurement after the failure of the probe. Due to lack of storage/work space, however, these analyses were performed at the shore base.

5.5.2 Sediment Grain Size

Sediment grain size analyses were performed using sieve and pipet procedures. Division of the sand fraction into phi classes was accomplished by graded sieving according to the methods of Holme and McIntyre (1971). Division of silt and clay (mud fraction) into phi categories was based on the pipet method (Folk, 1974).

Six individual replicates were processed from each station in Year-1 of the study. In Year-2 and Year-3, three sets of two replicates from each station (corresponding to the composited samples for trace metal and hydrocarbon analyses) were composited and processed.

A 25-g subsample of homogenized sediment was added to a dispersant solution of aqueous sodium metaphosphate (5 g/L) and allowed to stand overnight. The sample was agitated for 10 to 15 min on a Junior Orbital shaker and wet-sieved through a 0.063-mm screen. The mud fraction which passed through the sieve was suspended and 25-mL aliquots were removed at specific time intervals to determine the phi class categories. The aliquots were dried at 105°C overnight, cooled to room temperature, and weighed to the nearest 0.1 mg to determine silt and clay phi class intervals.

The sand fraction, which remained on the 0.063-mm sieve, was rinsed into a glass beaker and dried overnight. To divide the sand component into phi intervals, the dried sand was placed in a graduated series of nested sieves (screen sizes of 2 mm, 1 mm, 0.5 mm, 0.25 mm, 0.125 mm, and 0.063 mm) and shaken for 10 min on a Ro-Tap Testing Sieve Shaker.

For the purposes of data reporting and entry into the database, the -1 to >10 phi classes were recorded separately. They were also combined to generate gravel, sand, silt, and clay sediment size classes for data interpretation.

During the analysis, approximately every tenth sample was split and analyzed as duplicates to determine analytical variability. The results of these determinations are presented in Appendix B.

5.5.3 Total Organic Carbon (TOC)

TOC was determined with a Leco Model WR-12 carbon analyzer. A 150-250 mg homogenized, dried subsample was placed in a ceramic crucible and washed twice with 6N hydrochloric acid to remove carbonate carbon. If reaction was vigorous on the second wash, the sample was washed a third time with hydrochloric acid.

Following decarbonation, the sample was rinsed with distilled water until neutral and then dried at 45°C. Copper and zinc accelerators were added to the sample crucibles prior to combustion in an induction furnace. The evolved carbon dioxide was scrubbed of water, halide, and sulfur before calculation of the TOC in mg/g.

The carbon analyzer was calibrated daily with a series of calibration standards to provide a calibration curve covering the range of interest.

6.0 PRESENTATION OF RESULTS

6.1 INTRODUCTION

This section presents a three-year summary of the laboratory analyses for metals and hydrocarbons in marine sediments collected during the BSMP surveys. All unreduced (raw) data are included, by sampling year and station, on the enclosed diskette. A summary of the laboratory quality control data for the metals and hydrocarbon analyses is included in Section 6.3.

Riverine sediment and peat data for Year-2 and Year-3 are included in summary form with the data analysis (Section 7) and are completely listed on the data diskette. Because a complete three-year data set is only available for three animal species collected at three stations, the trace metal and hydrocarbon tissue data are included in summary tables in the data analysis section (Section 7) as well as on the diskette. The three-year auxiliary data, including grain size and total organic carbon concentrations for sediments are also included on the data diskette.

The analytical results are presented in separate subsections for trace metals and hydrocarbons. Tabulation of the data has been reduced to only parameters most relevant to interpretation, similar to the format of the Year-1 and Year-2 annual reports. A complete listing of each data set is additionally transmitted to the National Oceanic Data Center (NODC) as part of the final reporting requirements.

The sediment data are presented as two- or three-year geometric means with lower and upper 95-percent confidence limits. Because the trace metals analytical program was reoriented towards examining the mud fraction in Year-2 of the study (see Section 5), metals data for the mud fraction and the bulk sediments each represent two-year means. All organics data are three-year averages of the bulk sediments.

All sediment data are presented in tabular form, arranged by geographic groupings of stations (as defined in Section 7) from east to west within the Study Area, and accompanied by a station location map.

6.2 SEDIMENT TRACE METALS DATA

Metals were analyzed in bulk sediments from stations that were sampled in Year-1. The mud fraction and the bulk sediments from stations that were sampled in both Year-1 and Year-2 were analyzed for metals. Only the mud fraction of sediments from new stations sampled in Year-2 (e.g., the Camden Bay stations that were not accessible in Year-1), were analyzed for metals. In Year-3, only the sediment mud fractions were analyzed. Therefore, the trace metal data are reported separately for bulk sediments and mud fractions as two-year means.

Figures 6.1 through 6.6 present the two-year mean concentrations of metals in the bulk fraction of sediments from the 26 stations that were sampled in Year-1 and resampled in Year-2. Levels of all metals were generally higher in the East and West Harrison Bay areas (Figures 6.5 and 6.6) than in other regions of the Study Area. No geographic region, however, contained significantly lower metals concentrations than other areas. Mean barium concentrations in bulk sediment range from 128 to 704 µg/g (dry weight). Lead and copper levels are in the range of 6 to 29 µg/g, while chromium, vanadium, and zinc occur at concentrations between 22 and 143 µg/g.

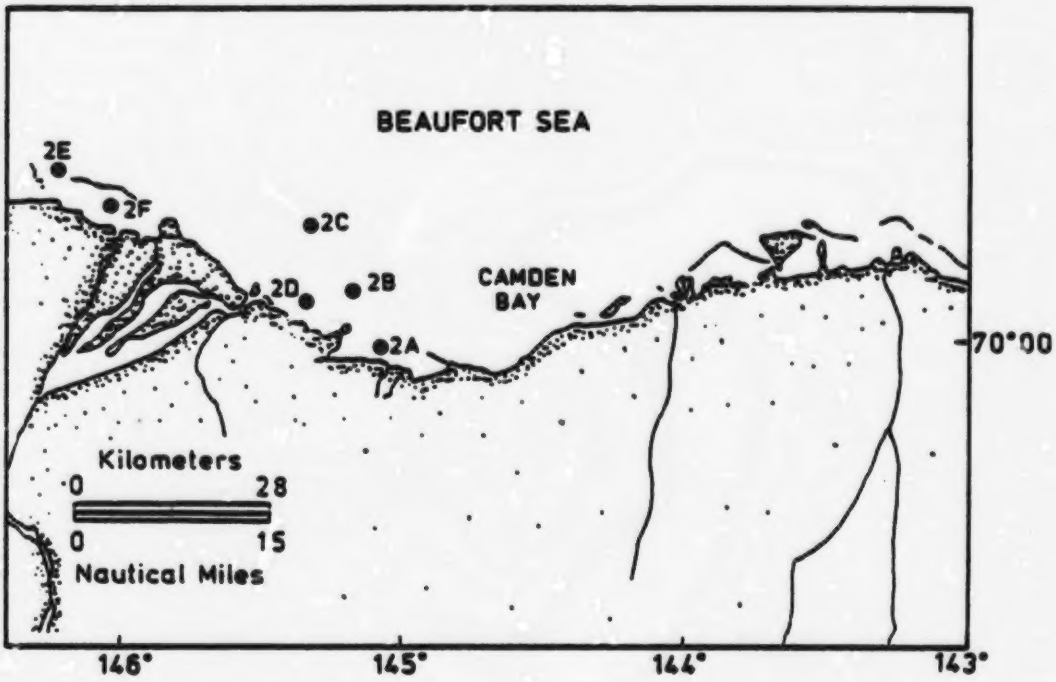
Figures 6.7 through 6.13 present the concentrations of metals in the mud fraction of sediments from the 39 stations that were sampled in Year-2 and Year-3. Concentrations of metals are generally higher in the mud fraction than in the bulk sediment, although a number of exceptions are noted for individual elements. The difference in mud fraction and bulk sediment metals concentrations is most pronounced in the Foggy Island Bay area (the "3" and "4" stations) and in the Endicott Field transect stations. Other Study Area regions show only a minimal difference between metals concentrations in the mud fraction and bulk sediment.

Mean barium concentrations in sediment mud fractions ranged from 95 to 698 µg/g. Lead and copper concentrations are in the range of 7 to 34 µg/g, while chromium, vanadium, and zinc levels range between 59 and 153 µg/g. Cadmium levels in mud fractions are universally low, ranging from 0.11 to 0.32 µg/g throughout the Study Area.

6.3 SEDIMENT HYDROCARBON DATA

GC-FID analyses for saturated hydrocarbons and GC/MS analyses for aromatics were performed on only the bulk sediments (although a limited comparative assessment of hydrocarbons in bulk sediment and mud fractions was conducted in Year-2; see discussion in Section 7.3). In addition to the GC-FID and GC/MS analyses, UV/F scans were performed on sediment samples collected in Year-1. Because of high background concentrations of fluorescing material in the sediments, the UV/F scans of sediment extracts were discontinued after the first year of the study.

The sediment hydrocarbon data are presented with the percent mud fraction and total organic carbon concentrations. All data represent three-year station means.



METALS (µg/g)[a]	STATIONS					
	2A	2B	2C	2D	2E	2F
Ba	-	-	-	-	161 (112;231)	175 (80;385)
Cr	-	-	-	-	55 (26;116)	41 (34;51)
V	-	-	-	-	82 (31;217)	68 (58;79)
Pb	-	-	-	-	9.3 (2.5;35)	7.3 (6.1;8.7)
Cu	-	-	-	-	21.2 (10.8;42)	12.7 (8.2;19.7)
Zn	-	-	-	-	62 (18;213)	53 (46;62)
Cd	-	-	-	-	0.2 (0.09;0.46)	0.21 (0.21;0.22)
% Mud	86 (75;98)	10 (9;11)	64 (51;79)	17 (13;23)	27 (7;98)	13 (11;15)

[a] All concentrations reported as geometric means with lower and upper 95% confidence limits in parentheses.

Dashes indicate no sample.

FIGURE 6.1 TWO-YEAR MEAN TRACE METAL CONCENTRATIONS AND PERCENT MUD IN WEST CAMDEN BAY AREA BULK SEDIMENTS.

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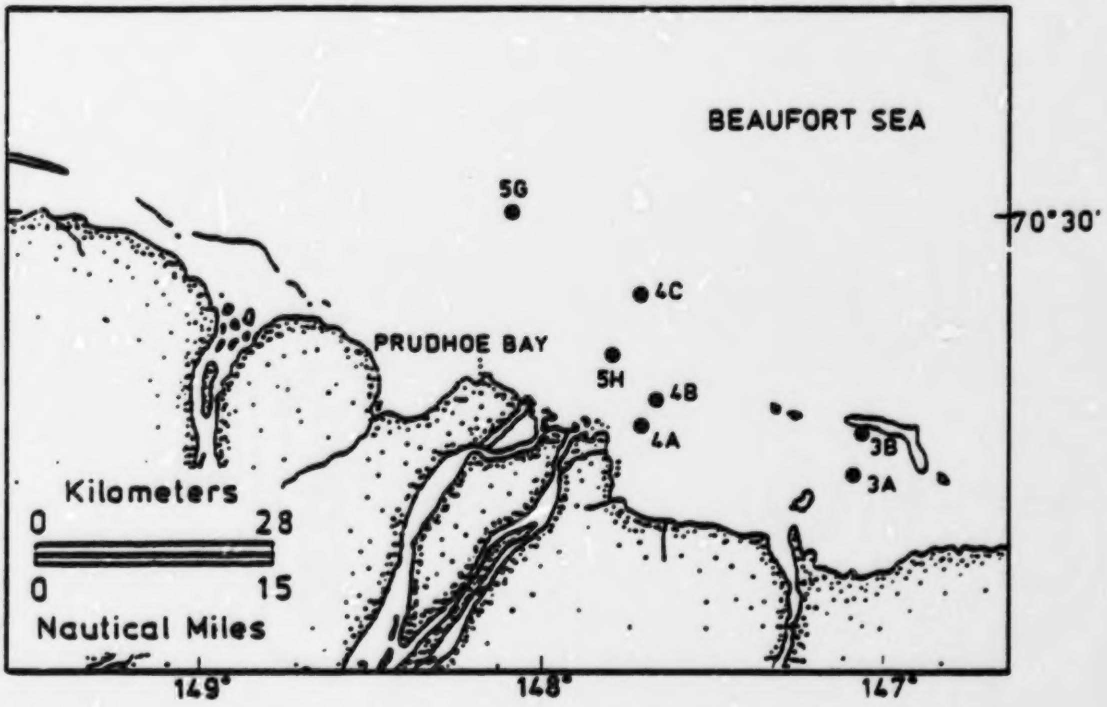

METALS (µg/g)[a]	STATIONS					
	3A	3B	4A	4B	4C	5G
Ba	286 (198;415)	347 (287;419)	269 (147;493)	185 (168;203)	270 (234;311)	271 (246;298)
Cr	49 (44;55)	58 (57;59)	44 (32;60)	30 (28;34)	37 (34;41)	35 (33;37)
V	83 (73;94)	99 (95;103)	78 (54;111)	46 (43;49)	59 (52;66)	61 (61;61)
Pb	7.9 (4.7;13)	8.0 (4.7;14)	8.6 (7.5;9.8)	5.9 (5.6;6.2)	6.3 (2.6;15)	6.7 (5.6;8.0)
Cu	19 (14;27)	24 (17;34)	19 (11;32)	12 (6.1;26)	14 (8.7;22)	11 (10;11)
Zn	61 (55;67)	70 (59;82)	59 (51;69)	39 (32;47)	38 (28;52)	43 (36;51)
Cd	0.16 (0.15;0.17)	0.16 (0.14;0.19)	0.12 (0.09;0.16)	0.19 (0.19;0.20)	0.07 (0.05;0.10)	0.10 (0.09;0.10)
% Mud	38 (28;51)	69 (64;74)	30 (27;33)	7 (5;12)	11 (6;20)	15 (11;22)

[a] All concentrations reported as geometric means with lower and upper 95% confidence limits in parentheses.

FIGURE 6.2 TWO-YEAR MEAN TRACE METAL CONCENTRATIONS AND PERCENT MUD IN THE FOGGY ISLAND BAY AREA BULK SEDIMENTS.

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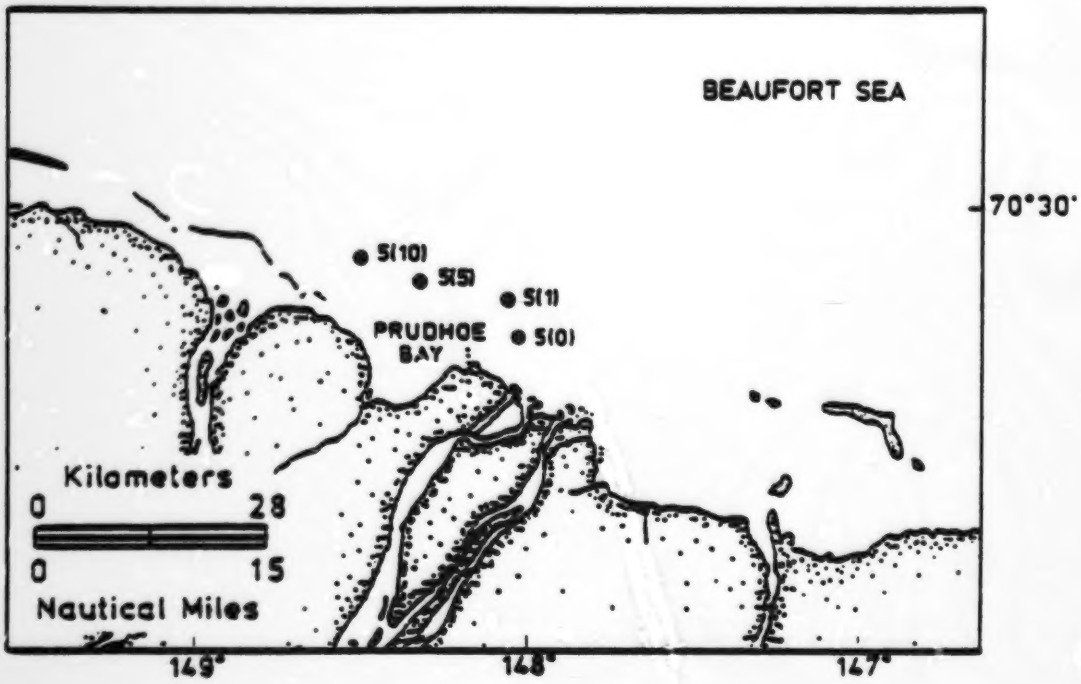

METALS (ug/g)[a]	STATIONS			
	5(0)	5(1)	5(5)	5(10)
Ba	-	209 (164;265)	257 (197;335)	137 (33;578)
Cr	-	22 (20;23)	37 (32;43)	39 (37;40)
V	-	42 (37;48)	63 (54;74)	64 (60;67)
Pb	-	6.3 (3.9;10)	6.6 (5.8;7.4)	5.7 (5.3;6.1)
Cu	-	7.6 (5.3;11)	13 (10;18)	14 (9.6;21)
Zn	-	37 (33;41)	51 (49;53)	53 (44;64)
Oil	-	0.11 (0.06;0.19)	0.18 (0.12;0.27)	0.24 (0.23;0.25)
% Mud	-	3 (1;12)	21 (11;39)	22 (15;33)

[a] All concentrations reported as geometric means with lower and upper 95% confidence limits in parentheses.

Dashes indicate no sample.

FIGURE 6.3 TWO-YEAR MEAN TRACE METAL CONCENTRATIONS AND PERCENT MUD IN THE ENDICOTT FIELD BULK SEDIMENTS.

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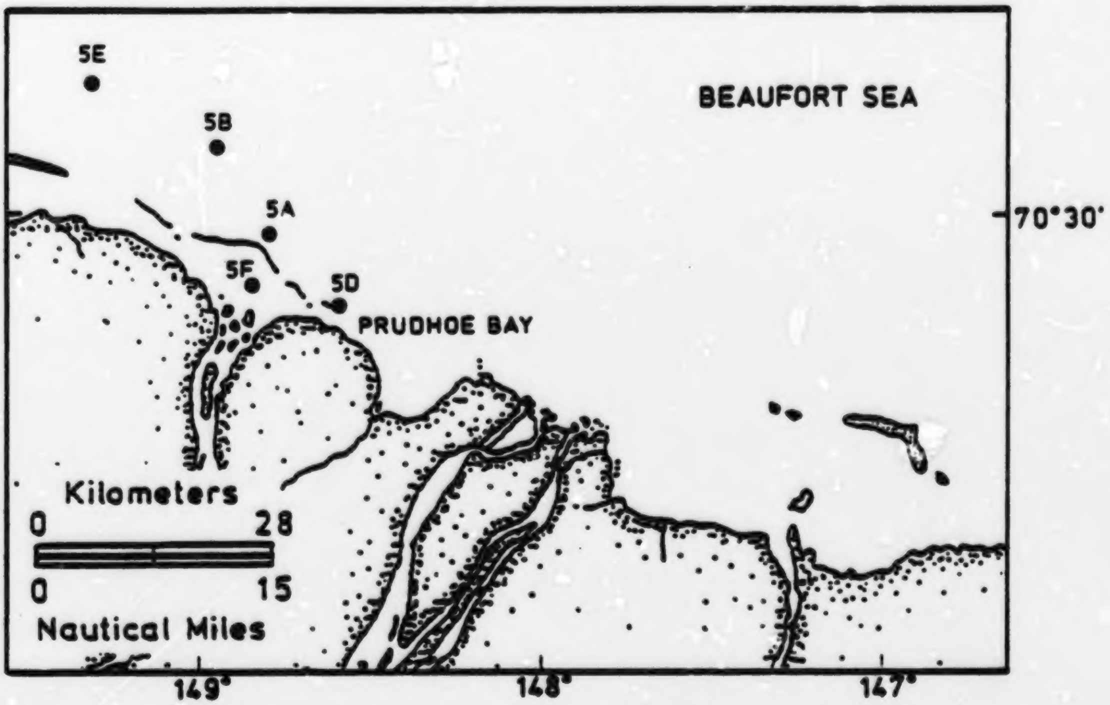

	STATIONS				
METALS (ug/g)[a]	5A	5B	5D	5E	5F
Ba	413 (236;724)	321 (118;871)	128 (16;1039)	393 (277;560)	304 (258;357)
Cr	51 (45;58)	39 (8;190)	52 (47;58)	50 (18;134)	42 (31;57)
V	83 (63;109)	70 (16;311)	85 (74;99)	92 (37;228)	66 (46;95)
Pb	8.7 (8.0;9.5)	8.2 (1.8;38)	8.4 (6.2;11)	9.8 (3.3;29)	7.2 (6.3;8.3)
Cu	19 (16;22)	12 (2.0;76)	21 (15;29)	18 (7.0;45)	13 (7.5;24)
Zn	63 (58;68)	46 (8;279)	77 (76;73)	60 (19;189)	58 (47;70)
Cd	0.22 (0.21;0.22)	0.07 (0.02;0.25)	0.25 (0.19;0.33)	0.12 (0.04;0.32)	0.18 (0.13;0.24)
% Mud	53 (39;72)	22 (3;148)	68 (61;74)	25 (12;55)	52 (42;64)

[a] All concentrations reported as geometric means with lower and upper 95% confidence limits in parentheses.

FIGURE 6.4 TWO-YEAR MEAN TRACE METAL CONCENTRATIONS AND PERCENT MUD IN THE KUPARUK RIVER AREA BULK SEDIMENTS.

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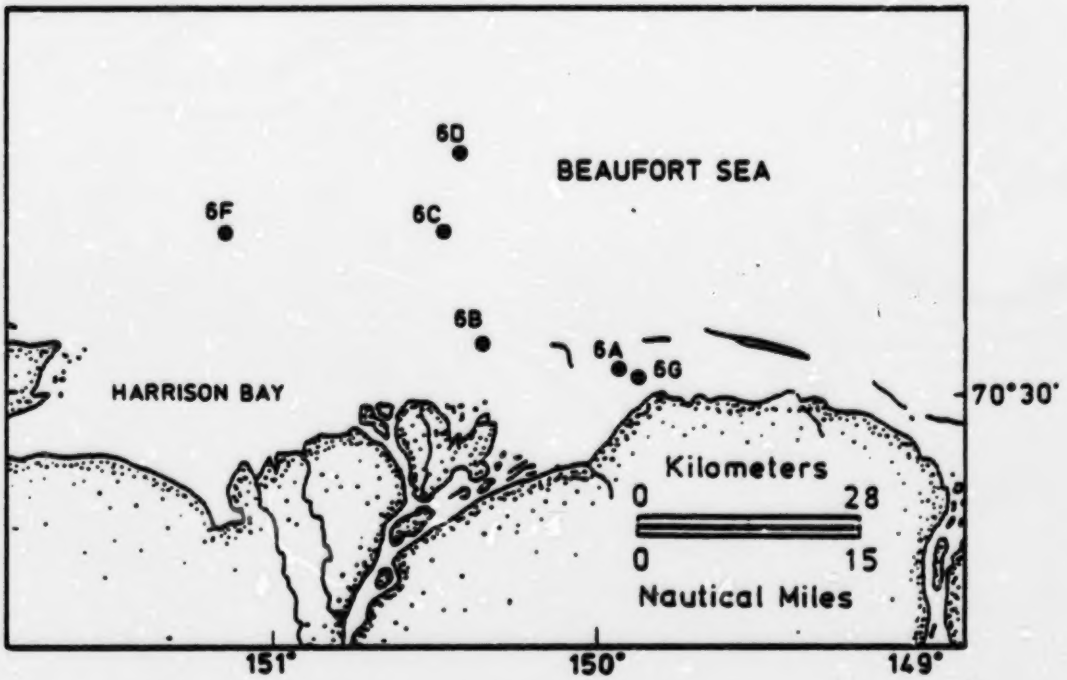

METALS ($\mu g/g$)[a]	STATIONS 6A	 6B	 6C	 6D	 6F
Ba	380 (370;390)	609 (411;901)	403 (367;444)	282 (282;282)	330 (257;423)
Cr	60 (59;60)	79 (58;106)	65 (62;68)	36 (32;40)	54 (41;72)
V	95 (88;104)	128 (91;180)	105 (87;128)	67 (65;70)	92 (68;123)
Pb	11 (6.6;19)	14 (11;19)	10 (6.6;16)	8.0 (6.2;10)	11 (8.5;13)
Cu	23 (22;24)	29 (19;46)	21 (20;22)	9.4 (8.6;10)	16 (11;25)
Zn	79 (63;99)	99 (77;127)	76 (58;100)	50 (42;59)	64 (57;72)
Cd	0.15 (0.10;0.23)	0.24 (0.16;0.34)	0.09 (0.04;0.18)	0.06 (0.06;0.06)	0.12 (0.11;0.13)
% Mud	73 (64;82)	84 (79;89)	34 (24;47)	14 (5;35)	46 (36;60)

[a] All concentrations reported as geometric means with lower and upper 95% confidence limits in parentheses.

FIGURE 6.5 TWO-YEAR MEAN TRACE METAL CONCENTRATIONS AND PERCENT MUD IN THE EAST HARRISON BAY BULK SEDIMENTS.

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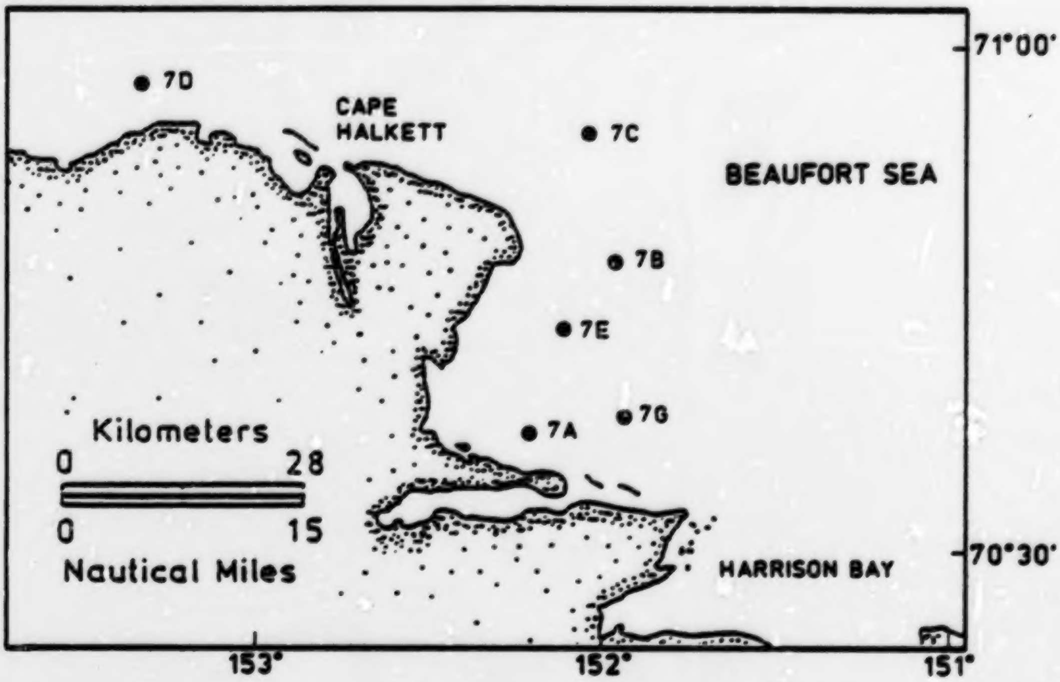

METALS (µg/g)[a]	STATIONS					
	7A	7B	7C	7D	7E	7G
Ba	704 (692;716)	470 (443;498)	533 (471;603)	-	582 (540;628)	621 (593;650)
Cr	67 (59;76)	51 (47;55)	81 (74;88)	-	62 (62;62)	43 (40;47)
V	88 (86;89)	63 (54;73)	143 (138;147)	-	92 (91;93)	68 (68;68)
Pb	11 (6.7;17)	8.2 (5.4;12)	17 (13;23)	-	11 (6.5;18)	12 (9.9;15)
Cu	14 (13;15)	8.3 (6.2;11)	28 (26;30)	-	18 (16;20)	11 (9.6;13)
Zn	80 (70;92)	50 (50;51)	102 (92;113)	-	73 (69;79)	58 (49;68)
Cd	0.10 (0.09;0.12)	0.06 (0.06;0.06)	0.14 (0.11;0.18)	-	0.14 (0.11;0.16)	0.08 (0.05;0.14)
% Mud	86 (75;98)	10 (9;11)	64 (51;79)	-	27 (7;98)	13 (11;15)

[a] All concentrations reported as geometric means with lower and upper 95% confidence limits in parentheses.

Dashes indicate no sample.

FIGURE 6.6 TWO-YEAR MEAN TRACE METAL CONCENTRATIONS AND PERCENT MUD IN THE WEST HARRISON BAY BULK SEDIMENTS.

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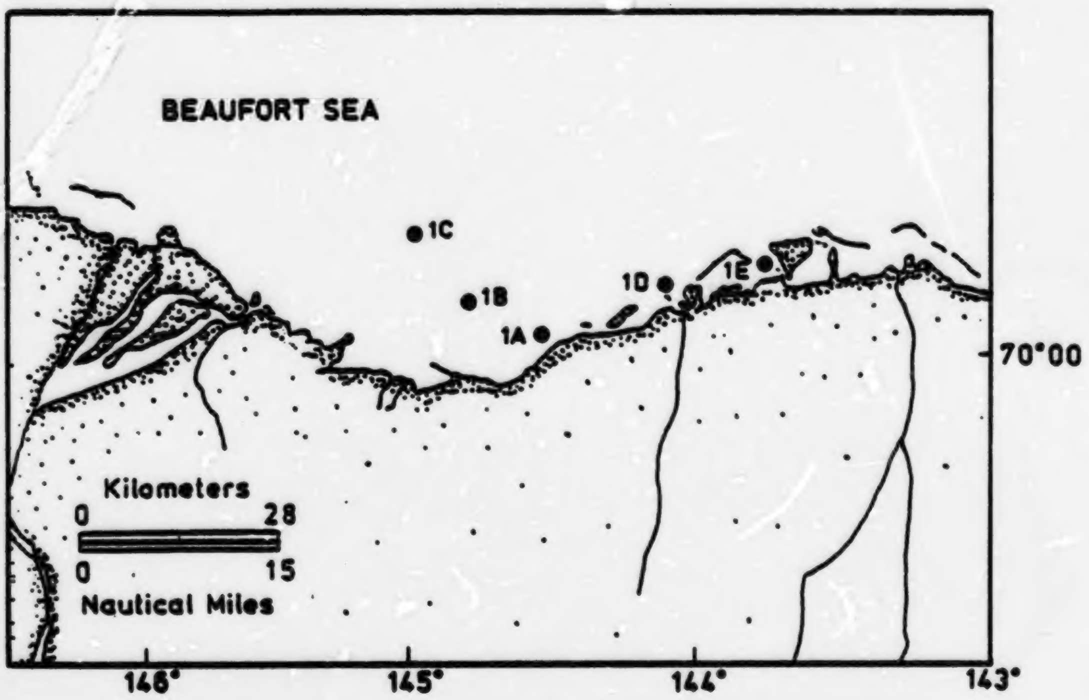

METALS (µg/g)[a]	STATIONS 1A	1B	1C	1D	1E
Ba	341 (232;501)	354 (147;907)	395 (249;626)	471 (403;551)	407 (290;572)
Cr	89 (74;107)	84 (74;95)	85 (82;89)	75 (65;87)	67 (64;69)
V	128 (118;139)	132 (122;141)	142 (140;144)	98 (88;110)	83 (69;101)
Pb	16 (11;24)	17 (16;18)	19 (18;19)	19 (12;32)	17 (9.9;28)
Cu	30 (29;30)	26 (23;29)	25 (23;27)	26 (25;27)	22 (16;29)
Zn	125 (79;197)	91 (84;98)	97 (83;114)	85 (84;87)	74 (57;95)
Cd	0.19 (0.15;0.25)	0.13 (0.11;0.15)	0.11 (0.05;0.23)	0.16 (0.10;0.24)	0.12 (0.10;0.15)

[a] All concentrations reported as geometric means with lower and upper 95% confidence limits in parentheses.

FIGURE 6.7 TWO-YEAR MEAN TRACE METAL CONCENTRATIONS IN THE MUD FRACTION OF EAST CAMDEN BAY AREA SEDIMENTS.

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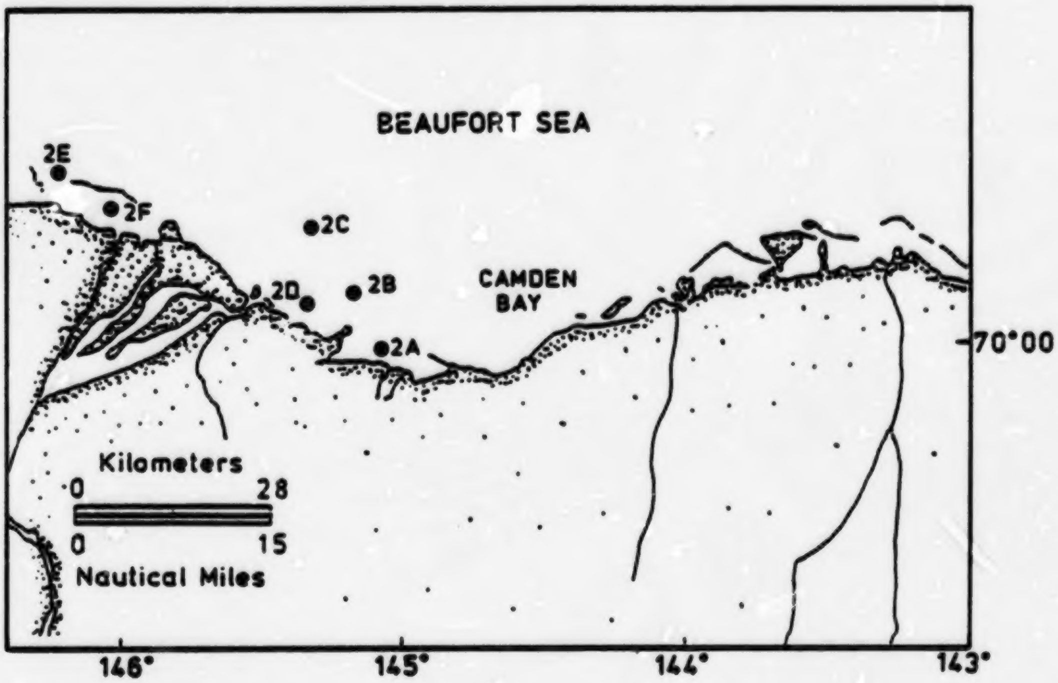

METALS (µg/g)[a]	STATIONS 2A	 2B	 2C	 2D	 2E	 2F
Ba	394 (263;591)	301 (229;394)	385 (216;686)	332 (326;339)	250 (102;614)	95 (12;761)
Cr	82 (63;106)	78 (76;79)	84 (81;88)	83 (77;63)	77 (73;81)	85 (59;122)
V	114 (113;115)	116 (98;138)	138 (131;146)	120 (107;133)	120 (99;145)	82 (70;95)
Pb	15 (14;17)	14 (11;18)	18 (15;21)	16 (11;22)	14 (11;18)	8.6 (5.4;14)
Cu	26 (23;29)	25 (19;33)	25 (21;29)	27 (22;34)	27 (22;33)	16 (9.8;25)
Zn	85 (70;104)	89 (77;104)	103 (100;107)	100 (85;118)	96 (72;128)	77 (74;80)
Cd	0.19 (0.18;0.20)	0.18 (0.16;0.20)	0.12 (0.08;0.19)	0.27 (0.24;0.30)	0.26 (0.22;0.32)	0.14 (0.04;0.52)

[a] All concentrations reported as geometric means with lower and upper 95% confidence limits in parentheses.

FIGURE 6.8 TWO-YEAR MEAN TRACE METAL CONCENTRATIONS IN THE MUD FRACTION OF WEST CAMDEN BAY AREA SEDIMENTS.

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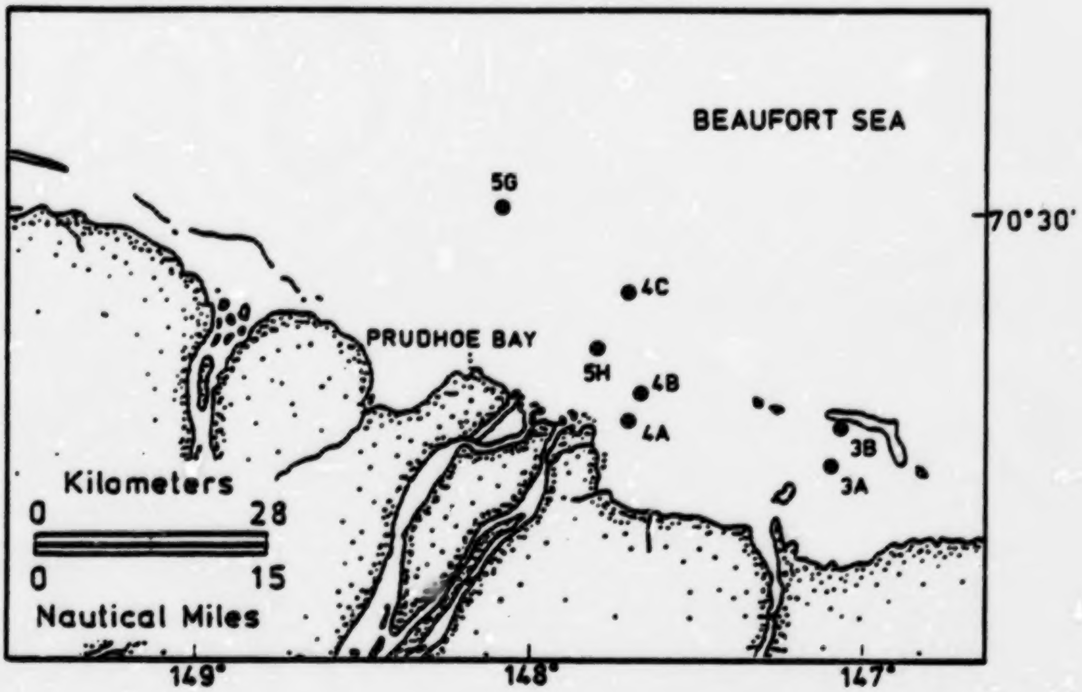

METALS (µg/g)[a]	STATIONS						
	3A	3B	4A	4B	4C	5G	5H
Ba	407 (329;503)	377 (358;396)	328 (239;450)	300 (225;399)	384 (237;623)	287 (268;308)	259 (138;485)
Cr	72 (64;82)	73 (61;88)	81 (76;86)	66 (52;84)	80 (76;83)	83 (75;92)	59 (57;83)
V	108 (107;110)	111 (99;124)	127 (125;130)	103 (93;114)	122 (122;123)	115 (110;120)	108 (106;109)
Pb	13 (10;16)	11 (11;11)	12 (8.9;17)	9.6 (7.8;12)	11 (4.9;27)	12 (8.6;16)	10 (8.3;13)
Cu	21 (17;24)	20 (18;21)	26 (24;29)	19 (19;19)	22 (20;25)	19 (18;19)	20 (18;22)
Zn	85 (82,88)	83 (77;89)	104 (104;105)	87 (78;98)	88 (77;101)	85 (82;88)	82 (71;94)
Cd	0.16 (0.14;0.20)	0.17 (0.15;0.20)	0.29 (0.20;0.42)	0.19 (0.19;0.20)	0.16 (0.14;0.18)	0.15 (0.15;0.15)	0.22 (0.20;0.23)

[a] All concentrations reported as geometric means with lower and upper 95% confidence limits in parentheses.

FIGURE 6.9 TWO-YEAR MEAN TRACE METAL CONCENTRATIONS IN THE MUD FRACTION OF FOGGY ISLAND BAY AREA SEDIMENTS.

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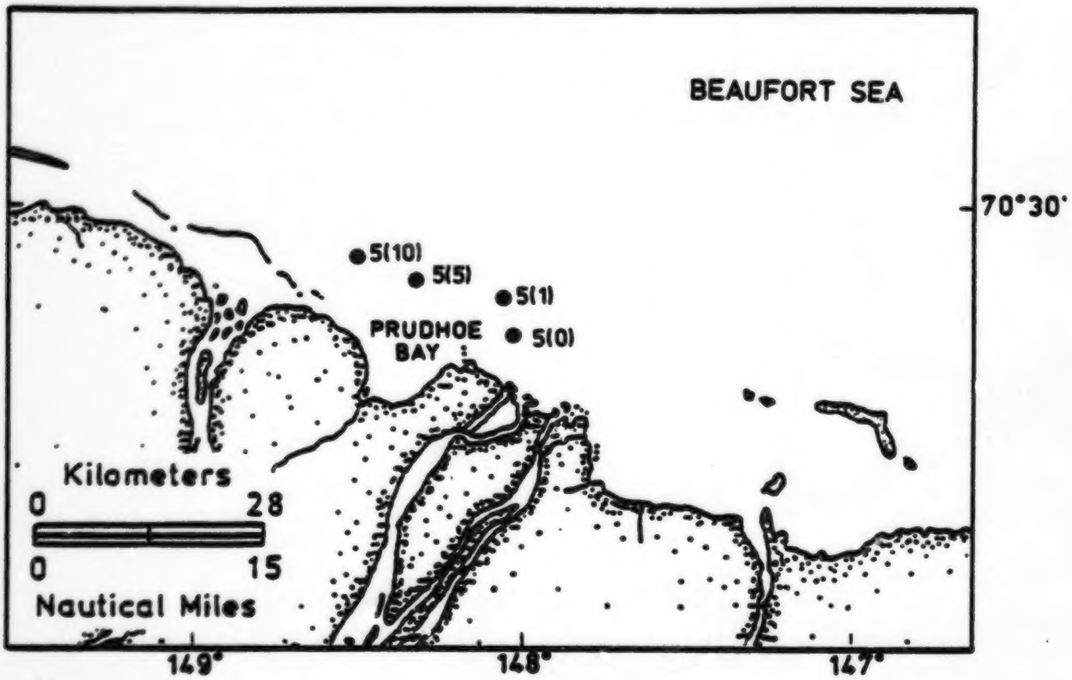

METALS (µg/g)[a]	STATIONS			
	5(0)	5(1)	5(5)	5(10)
Ba	241 (184;315)	250 (202;310)	356 (314;404)	329 (232;468)
Cr	61 (43;86)	69 (68;69)	75 (65;86)	68 (57;81)
V	98 (92;105)	84 (70;101)	108 (105;112)	98 (97;99)
Pb	9.2 (8.7;9.6)	9.0 (5.6;14)	11 (11;11)	9.7 (9.2;10)
Cu	19 (18;20)	15 (13;17)	20 (18;22)	18 (16;20)
Zn	85 (72;100)	71 (59;86)	81 (72;91)	75 (69;82)
Cd	0.25 (0.19;0.33)	0.32 (0.20;0.52)	0.20 (0.17;0.23)	0.18 (0.13;0.25)

[a] All concentrations reported as geometric means with lower and upper 95% confidence limits in parentheses.

FIGURE 6.10 TWO-YEAR MEAN TRACE METAL CONCENTRATIONS IN THE MUD FRACTION OF ENDICOTT FIELD SEDIMENTS.

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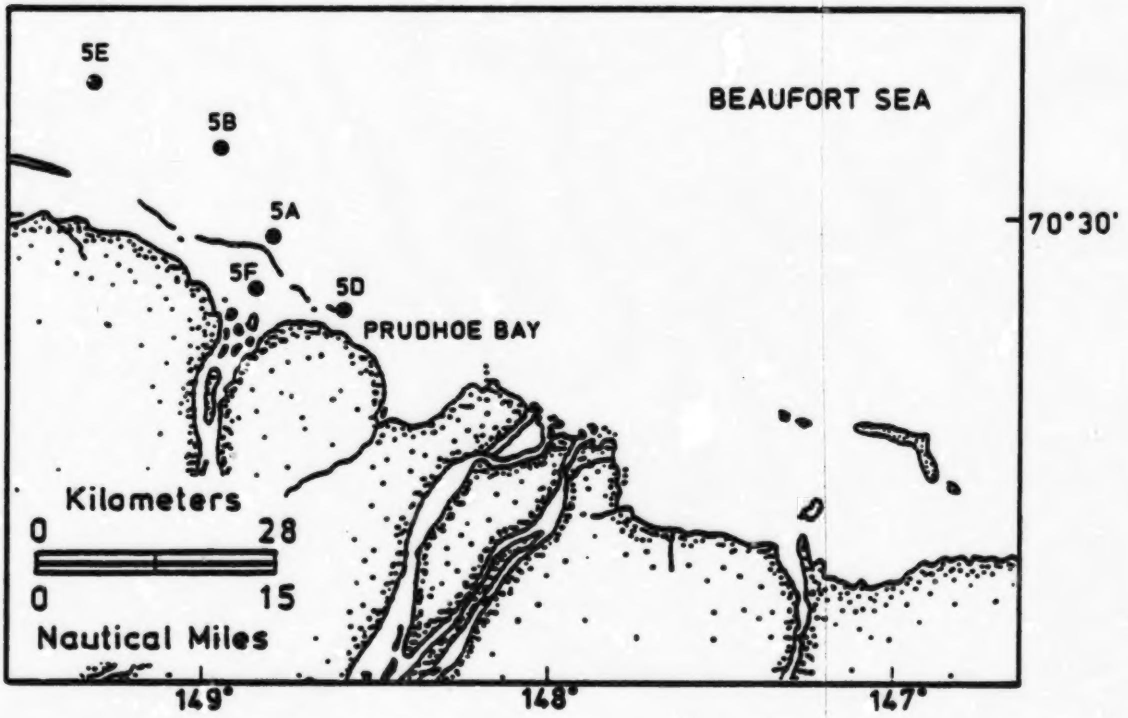

METALS (µg/g)[a]	STATIONS 5A	5B	5D	5E	5F
Ba	398 (385;411)	330 (324;336)	220 (113;428)	313 (287;342)	152 (35;654)
Cr	72 (57;90)	87 (77;99)	72 (53;98)	85 (74;97)	66 (48;91)
V	106 (95;118)	144 (138;152)	90 (86;94)	147 (143;151)	86 (73;102)
Pb	11 (9.9;12)	14 (10;19)	6.6 (4.3;10)	14 (11;18)	7.3 (5.4;9.7)
Cu	19 (18;20)	27 (27;28)	16 (15;18)	28 (27;30)	14 (11;18)
Zn	79 (75;83)	121 (90;164)	79 (73;85)	98 (93;105)	80 (69;93)
Cd	0.19 (0.17;0.21)	0.14 (0.13;0.16)	0.23 (0.14;0.36)	0.18 (0.13;0.24)	0.22 (0.17;0.30)

[a] All concentrations reported as geometric means with lower and upper 95% confidence limits in parentheses.

FIGURE 6.11 TWO-YEAR MEAN TRACE METAL CONCENTRATIONS IN THE MUD FRACTION OF THE KUPARUK RIVER AREA SEDIMENTS.

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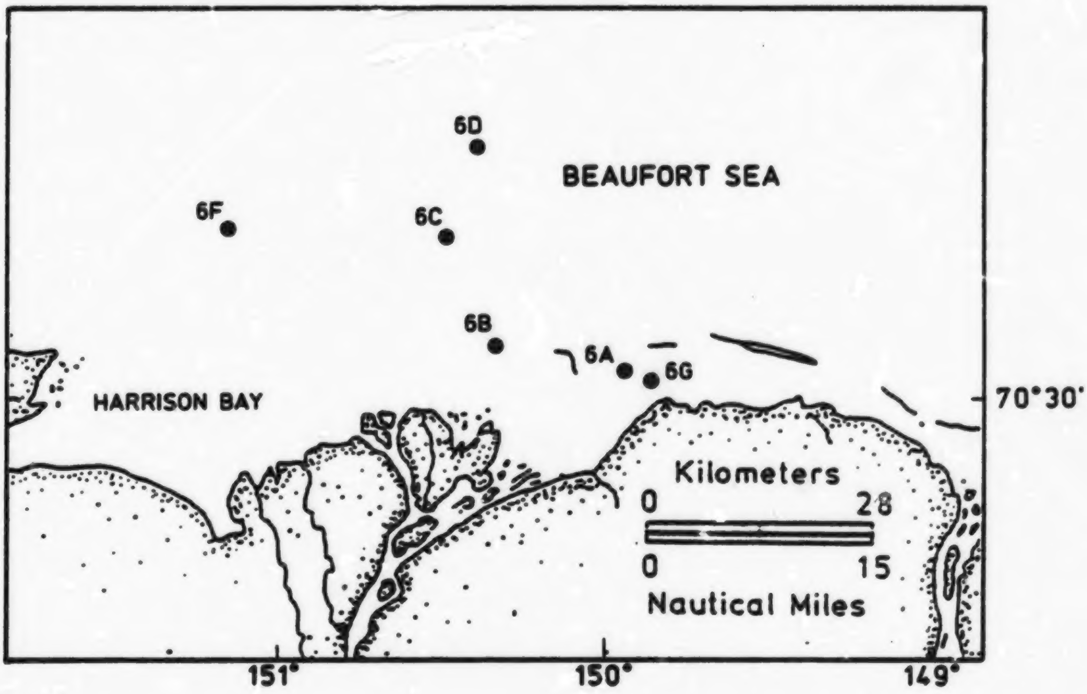

METALS (µg/g)[a]	STATIONS 6A	 6B	 6C	 6D	 6F	 6G
Ba	342 (319;366)	496 (449;548)	312 (191;509)	333 (285;390)	266 (204;346)	207 (107;400)
Cr	84 (68;103)	99 (82;120)	93 (85;101)	89 (72;109)	100 (79;125)	78 (51;120)
V	111 (106;117)	147 (139;155)	153 (150;156)	142 (125;161)	138 (118;160)	100 (96;104)
Pb	12 (8.3;17)	14 (14;16)	15 (14;17)	14 (14;14)	14 (14;14)	9.1 (5.7;14)
Cu	21 (18;25)	34 (30;40)	29 (27;31)	25 (23;28)	24 (19;31)	18 (16;21)
Zn	94 (83;106)	121 (113;130)	108 (99;117)	98 (93;103)	93 (92;94)	87 (73;105)
Cd	0.19 (0.15;0.23)	0.23 (0.20;0.26)	0.14 (0.10;0.20)	0.11 (0.06;0.19)	0.14 (0.14;0.15)	0.19 (0.12;0.29)

[a] All concentrations reported as geometric means with lower and upper 95% confidence limits in parentheses.

FIGURE 6.12 TWO-YEAR MEAN TRACE METAL CONCENTRATIONS IN THE MUD FRACTION OF EAST HARRISON BAY SEDIMENTS.

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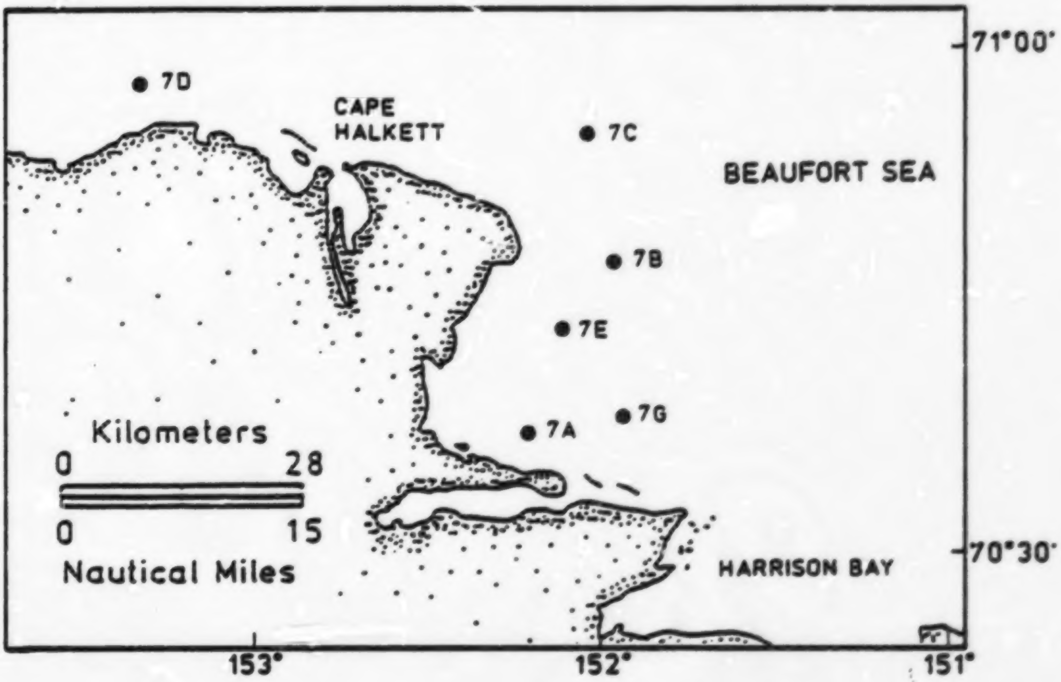

	STATIONS					
METALS (µg/g)[a]	7A	7B	7C	7D	7E	7G
Ba	698 (5654;863)	459 (233;903)	373 (221;628)	420 (319;554)	568 (302;1067)	676 (591;774)
Cr	82 (63;106)	78 (76;79)	84 (81;88)	83 (77;88)	77 (73;81)	85 (59;122)
V	114 (113;115)	116 (98;138)	138 (131;146)	120 (107;133)	120 (99;145)	82 (70;95)
Pb	15 (14;17)	14 (11;18)	18 (15;21)	16 (11;22)	14 (11;18)	8.6 (5.4;14)
Cu	26 (23;29)	25 (19;33)	25 (21;29)	27 (22;34)	27 (22;33)	16 (9.8;25)
Zn	85 (70;104)	89 (77;104)	103 (100;107)	100 (85;118)	96 (72;128)	77 (74;80)
Cd	0.19 (0.18;0.20)	0.18 (0.16;0.20)	0.12 (0.08;0.19)	0.27 (0.24;0.30)	0.26 (0.22;0.32)	0.14 (0.04;0.52)

[a] All concentrations reported as geometric means with lower and upper 95% confidence limits in parentheses.

FIGURE 6.13 TWO-YEAR MEAN TRACE METAL CONCENTRATIONS IN THE MUD FRACTION OF WEST HARRISON BAY SEDIMENTS.

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6.3.1 Saturated Hydrocarbons in Sediments

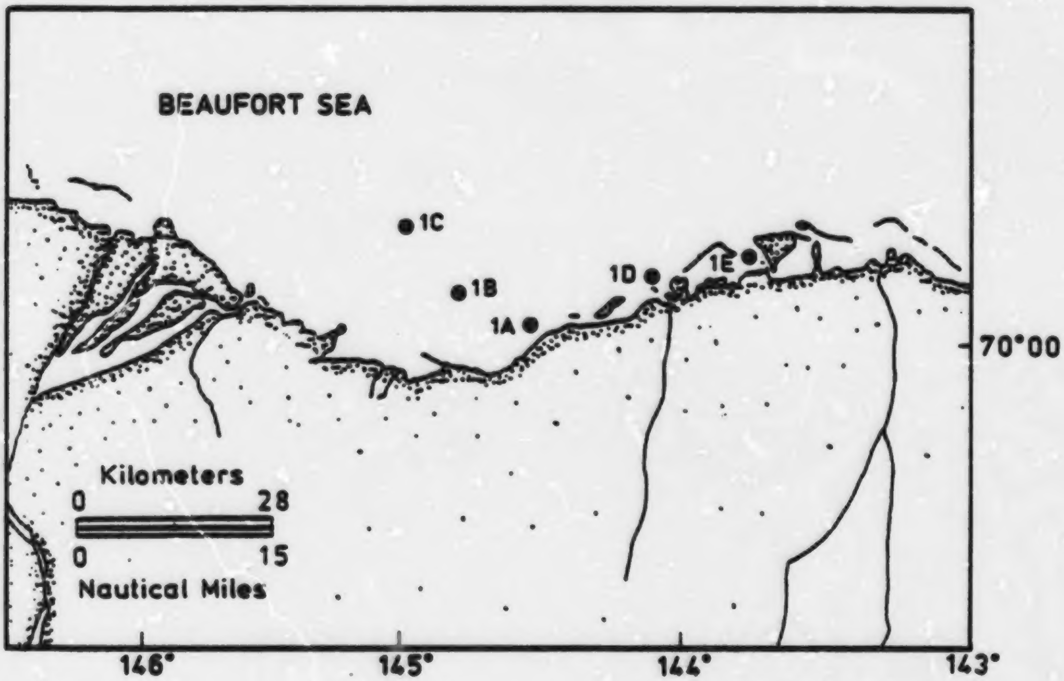
Figures 6.14 through 6.20 present the mean saturated hydrocarbon parameters for the 39 stations sampled in the survey. Mean percent mud (silt + clay) and TOC (mg/g dry weight) are included for comparison on all figures. Total alkanes (TALK), the n-C10 through n-C34 compounds, range from 0.78 to 19 μg/g (dry weight) throughout the Study Area. The low molecular weight alkanes (LALK), or n-C10 through n-C20 compounds, range from 0.20 to 2.5 μg/g. The sediment concentrations of pristane are low and range from 0.01 to 0.23 μg/g, whereas phytane concentrations are even lower, ranging from detection limits to 0.11 μg/g. Total resolved plus unresolved hydrocarbon concentrations (TOT) range from 2 to 52 μg/g. Sediment mud content varies widely and ranges between 3 and 86 percent. Total organic carbon is less variable and ranges from 3.4 to 18 mg/g.

In general, the highest saturated hydrocarbon concentrations are associated with sediments from the Harrison Bay area. Concentrations are generally lower in other regions of the Study Area. However, there is sufficient variation in saturated hydrocarbon concentrations within all geographical areas that considerable overlap in saturated hydrocarbon levels can be found throughout the BSMP Study Area.

The data for the East and West Camden Bay areas are presented in Figures 6.14 and 6.15, respectively. The nearshore-to-offshore transect stations (1A, 1B, and 1C in Figure 6.14 and 2A, 2B, and 2C in Figure 6.15) do not show a gradient for any of the parameters. No significant trends are observed among the other Camden Bay stations.

Figure 6.16 presents the saturated hydrocarbon data for the Foggy Island Bay area. The highest values for all parameters are observed at Station 3B and the lowest occur at Station 4B. No concentration gradients are associated with the transect stations 4A, 4B, and 4C.

The central part of the Study Area is divided into two groupings--the Endicott Field stations (Figure 6.17) and the Kuparuk River Bay area (Figure 6.18). In these regions, the highest concentrations are found in sediments at Stations 5D and 5E. Station 5D is an inshore station located behind a barrier island, whereas Station 5E is an offshore station. The Endicott Field transect stations do not show a gradient away from this area of activity. Instead, higher levels are associated with sediments from Stations 5(5) and 5(10), while lower concentrations are found in Station 5(0) and 5(1) sediments. Sediment hydrocarbon concentrations at these transect stations appear related to percent mud and TOC concentrations.



SATURATED HYDROCARBONS (µg/g)[a]	STATIONS				
	1A	**1B**	**1C**	**1D**	**1E**
TALK	6.6 (5.9;7.5)	2.4 (2.1;2.7)	6.5 (6.3;6.7)	3.2 (2.8;3.5)	5.3 (1.1;26)
LALK	0.50 (0.50;0.51)	0.37 (0.29;0.36)	1.0 (0.96;1.1)	0.24 (0.16;0.35)	0.48 (0.11;2.1)
Pris	0.04 (0.03;0.06)	0.03 (0.03;0.04)	0.12 (0.10;0.15)	0.01 (0.01;0.01)	0.02 (0.01;0.04)
Phyt	0.02 (0.02;0.03)	0.02 (0.01;0.02)	0.08 (0.07;0.09)	0.01 (0.01;0.01)	0.01 (0.0;0.01)
TOT	15 (13;18)	4.9 (4.6;5.1)	20.0 (13;30)	14 (1.7;120)	11 (2.6;45)
% Mud	64 (57;72)	13 (11;15)	70 (70;70)	24 (11;51)	50 (14;169)
TOC (mg/g)	9.6 (6.7;14)	7.2 (5.8;9.0)	8.9 (7.8;10)	5.9 (4.7;7.4)	6.8 (2.4;19)

[a] All concentrations reported as geometric means with lower and upper 95% confidence limits in parentheses.

FIGURE 6.14 THREE-YEAR MEAN SATURATED HYDROCARBON CONCENTRATIONS, PERCENT MUD, AND TOTAL ORGANIC CARBON IN EAST CAMDEN BAY AREA BULK SEDIMENTS.

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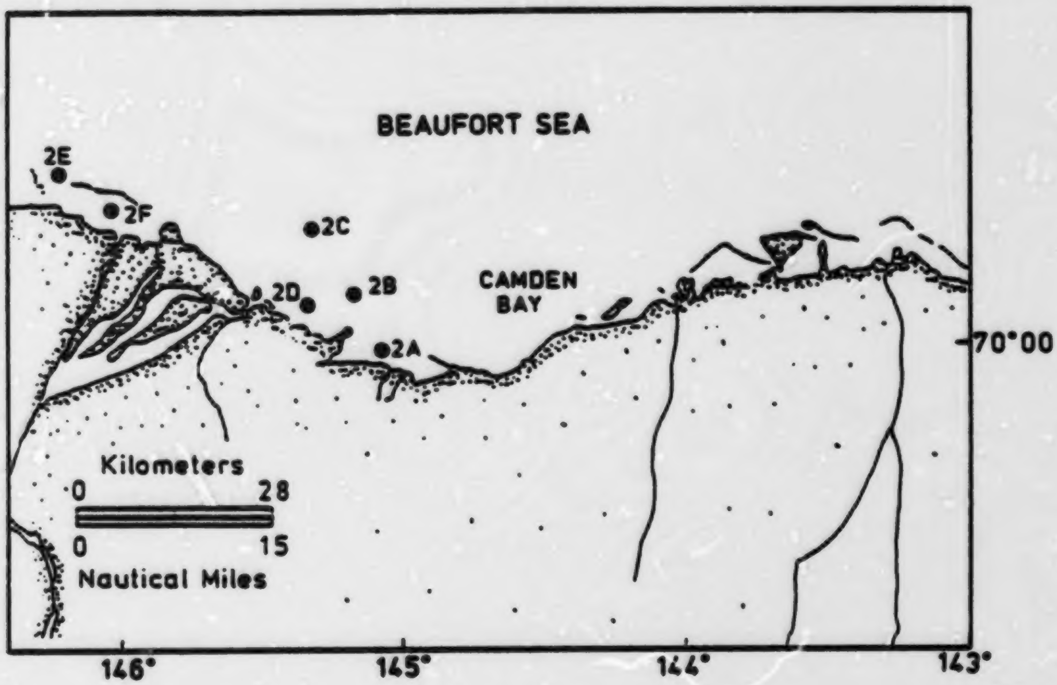

SATURATED HYDROCARBONS (μg/g)[a]	STATIONS 2A	2B	2C	2D	2E	2F
TALK	9.3 (8.7;9.9)	1.7 (0.6;4.5)	6.0 (5.1;7.0)	2.8 (1.4;5.5)	2.4 (0.7;7.7)	1.0 (0.7;1.5)
LALK	1.4 (1.1;1.7)	0.24 (0.13;0.46)	0.95 (0.80;1.1)	0.40 (0.17;0.90)	0.49 (0.22;1.1)	0.32 (0.24;0.44)
Pris	0.12 (0.07;0.18)	0.03 (0.02;0.03)	0.11 (0.11;0.11)	0.03 (0.01;0.09)	0.03 (0.01;0.11)	0.02 (0.01;0.03)
Phyt	0.07 (0.05;0.09)	0.01 (0.0;0.03)	0.07 (0.06;0.08)	0.02 (0.01;0.04)	0.02 (0.0;0.06)	0.01 (0.01;0.01)
TOF	22 (20;24)	4.9 (3.8;6.4)	14 (13;15)	9.8 (3.8;25)	7.9 (7.9;25)	3.7 (1.7;8.1)
% Mud	86 (75;98)	10 (9;11)	64 (51;79)	17 (13;23)	27 (7;98)	13 (11;15)
TOC (mg/g)	13 (9.2;19)	5.3 (1.5;18)	8.7 (6.2;12)	7.4 (5.0;11)	5.0 (2.2;12)	4.3 (3.0;6.0)

[a] All concentrations reported as geometric means with lower and upper 95% confidence limits in parentheses.

FIGURE 6.15 THREE-YEAR MEAN SATURATED HYDROCARBON CONCENTRATIONS, PERCENT MUD, AND TOTAL ORGANIC CARBON IN WEST CAMDEN BAY AREA BULK SEDIMENTS.

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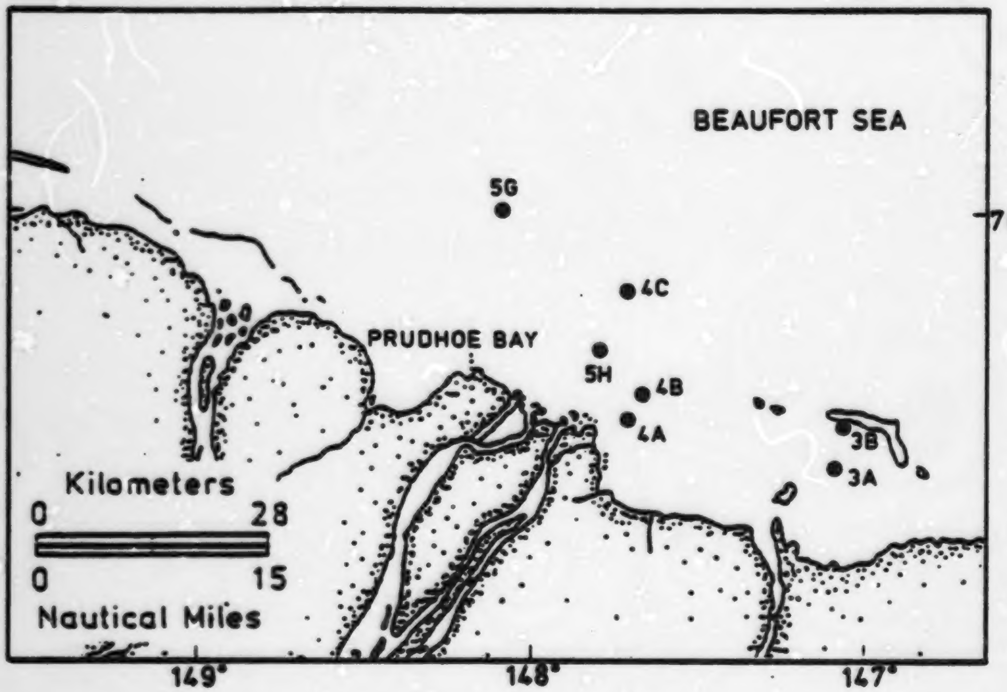

SATURATED HYDROCARBONS (µg/g)[a]	STATIONS						
	3A	3B	4A	4B	4C	5G	5H
TALK	2.9 (2.4;3.5)	5.8 (4.3;7.7)	3.2 (3.0;3.4)	1.3 (0.9;1.9)	2.3 (1.7;3.0)	2.2 (1.7;3.0)	3.5 (3.0;4.1)
LALK	0.43 (0.34;0.54)	0.[illegible] (0.72;1.1)	0.57 (0.51;0.63)	0.30 (0.21;0.43)	0.47 (0.33;0.68)	0.47 (0.30;0.74)	0.60 (0.41;0.86)
Pris	0.03 (0.02;0.05)	0.06 (0.04;0.08)	0.04 (0.03;0.06)	0.02 (0.01;0.02)	0.03 (0.03;0.03)	0.04 (0.02;0.06)	0.03 (0.03;0.03)
Phyt	0.02 (0.01;0.02)	0.03 (0.02;0.04)	0.02 (0.02;0.02)	0.01 (0.01;0.01)	0.01 (0.01;0.02)	0.02 (0.01;0.02)	0.01 (0.01;0.01)
TOT	7.7 (4.7;13)	17 (13;21)	9.6 (7.3;13)	4.0 (3.6;4.4)	7.5 (6.3;8.9)	7.2 (4.7;11)	9.6 (7.9;11)
% Mud	38 (28;51)	69 (64;74)	30 (27;33)	8 (5;12)	11 (6;20)	15 (11;22)	18 (13;24)
TOC (mg/g)	8.6 (6.8;11)	10 (9.1;11)	7.8 (4.4;13)	3.4 (2.5;4.5)	4.9 (2.2;11)	5.6 (4.4;7.2)	9.2 (4.4;19)

[a] All concentrations reported as geometric means with lower and upper 95% confidence limits in parentheses.

FIGURE 6.16 THREE-YEAR MEAN SATURATED HYDROCARBON CONCENTRATIONS, PERCENT MUD, AND TOTAL ORGANIC CARBON IN FOGGY ISLAND BAY AREA BULK SEDIMENTS.

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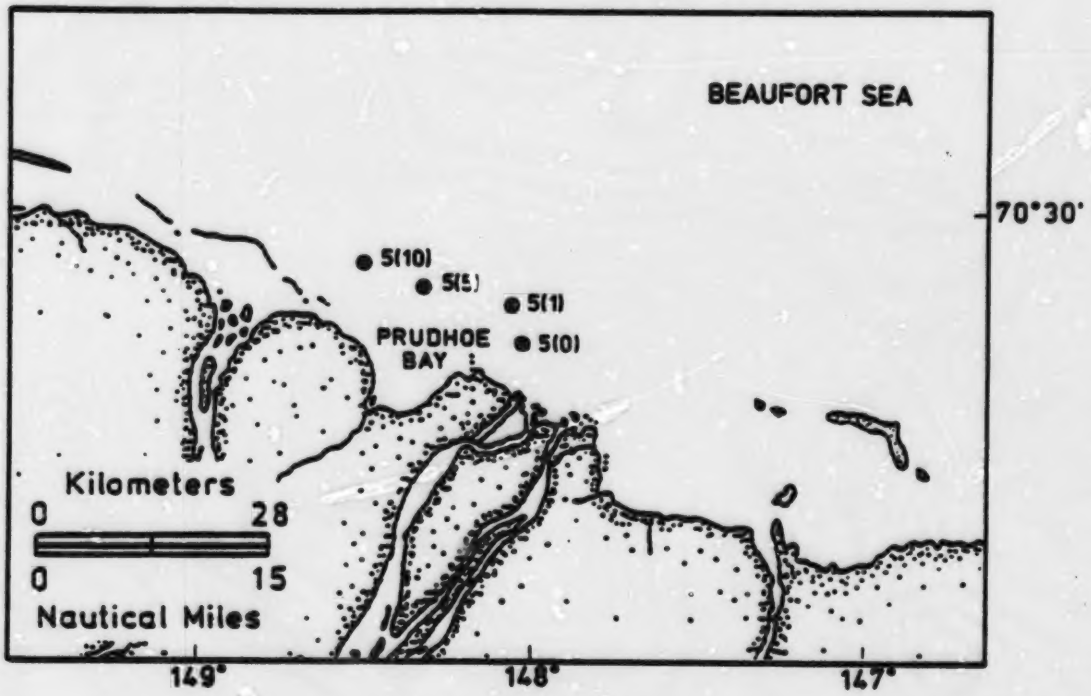

SATURATED HYDROCARBONS (µg/g)[a]	STATIONS 5(0)	5(1)	5(5)	5(10)
TALK	1.4 (1.3;1.4)	0.78 (0.49;1.2)	2.4 (1.7;3.5)	2.8 (2.1;3.7)
LALK	0.27 (0.24;0.30)	0.20 (0.13;0.32)	0.44 (0.29;0.67)	0.46 (0.27;0.77)
Pris	0.02 (0.01;0.02)	0.01 (0.01;0.02)	0.03 (0.02;0.06)	0.03 (0.02;0.05)
Phyt	0.01 (0.01;0.01)	< D.L.[b]	0.02 (0.01;0.03)	0.02 (0.01;0.02)
TOT	2.7 (2.0;3.6)	2.0 (0.84;4.6)	7.2 (4.0;13)	9.8 (7.0;14)
% Mud	7 (3;13)	3 (1;12)	21 (11;39)	22 (15;33)
TOC (mg/g)	3.4 (2.5;4.5)	3.5 (2.5;4.9)	5.7 (3.6;8.9)	7.2 (4.8;11)

[a] All concentrations reported as geometric means with lower and upper 95% confidence limits in parentheses.

[b] Less than detection limit.

FIGURE 6.17 THREE-YEAR MEAN SATURATED HYDROCARBON CONCENTRATIONS, PERCENT MUD, AND TOTAL ORGANIC CARBON IN ENDICOTT FIELD BULK SEDIMENTS.

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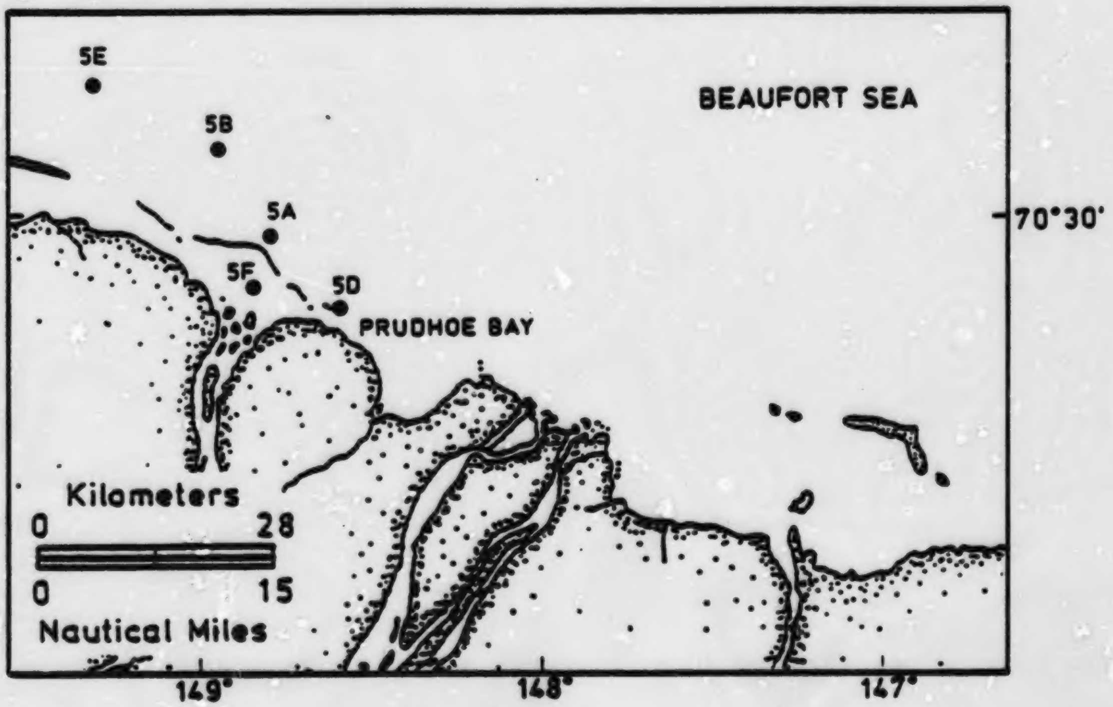

SATURATED HYDROCARBONS (µg/g)[a]	STATIONS				
	5A	5B	5D	5E	5F
TALK	4,8 (3.8;6.1)	3.1 (7.8;12)	8.8 (7.8;10)	5.9 (2.3;15)	7.2 (3.2;16)
LALK	0.78 (0.53;1.2)	0.67 (0.28;1.6)	0.96 (0.85;1.1)	1.2 (0.61;2.2)	0.96 (0.59;1.5)
Pris	0.06 (0.04;0.08)	0.05 (0.01;0.21)	0.06 (0.05;0.08)	0.11 (0.04;0.28)	0.05 (0.03;0.10)
Phyt	0.03 (0.02;0.04)	0.03 (0.0;0.16)	0.03 (0.03;0.04)	0.05 (0.02;0.16)	0.03 (0.02;0.04)
TOR	12 (10;14)	12 (2.8;53)	29 (26;34)	29 (7.7:107)	4.3 (9.5;20)
% Mud	53 (39;72)	22 (3;148)	68 (61;74)	25 (12;55)	52 (42;64)
TOC (mg/g)	9.6 (6.3;14)	5.2 (2.0;13)	18 (11;29)	8.1 (5.9;11)	12 (7.3;18)

[a] All concentrations reported as geometric means with lower and upper 95% confidence limits in parentheses.

FIGURE 6.18 THREE-YEAR MEAN SATURATED HYDROCARBON CONCENTRATIONS, PERCENT MUD, AND TOTAL ORGANIC CARBON IN THE KUPARUK RIVER AREA BULK SEDIMENTS.

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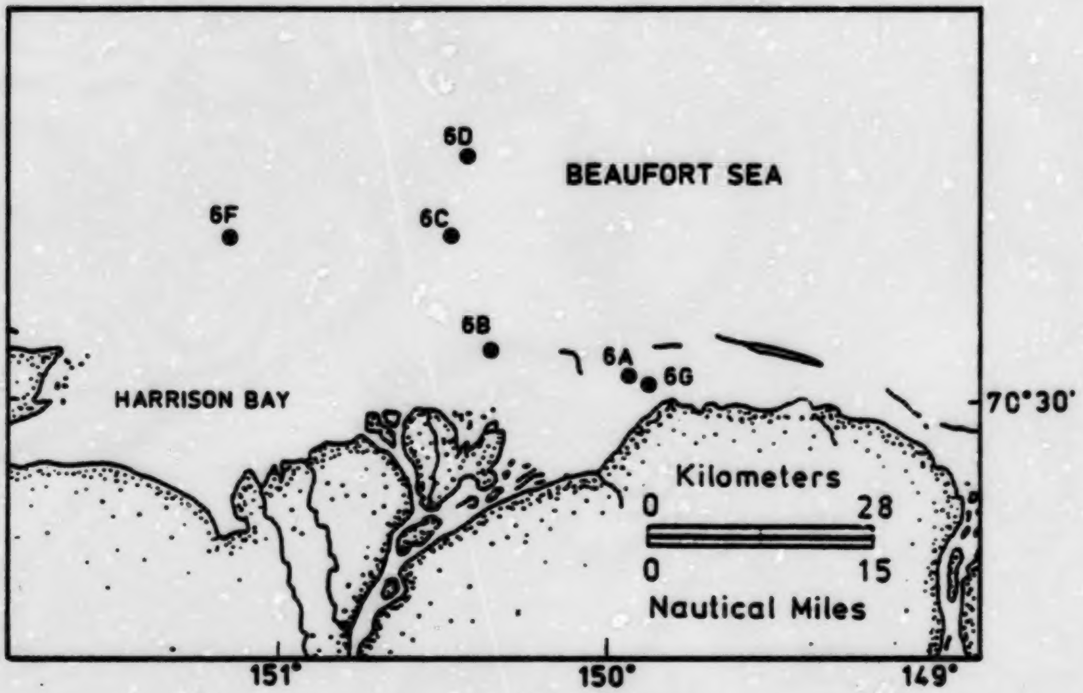

SATURATED HYDROCARBONS (µg/g)[a]	STATIONS					
	6A	6B	6C	6D	6F	6G
TALK	9.6 (8.3;11)	19 (10;36)	5.8 (3.8;8.9)	3.1 (1.6;6.3)	6.2 (4.7;8.3)	14 (7.1;29)
LALK	1.5 (0.88;2.4)	2.5 (0.96;6.5)	0.95 (0.58;1.6)	0.57 (0.21;1.5)	0.95 (0.63;1.4)	1.4 (0.58;3.4)
Pris	0.10 (0.08;0.13)	0.23 (0.09;0.59)	0.08 (0.05;0.15)	0.04 (0.02;0.08)	0.08 (0.06;0.10)	0.09 (0.04;0.17)
Phyt	0.05 (0.04;0.05)	0.11 (0.03;0.32)	0.03 (0.02;0.07)	0.02 (0.01;0.04)	0.04 (0.03;0.05)	0.06 (0.05;0.07)
TOT	41 (18;94)	52 (33;81)	28 (11;72)	8.4 (4.5;16)	18 (13;26)	34 (11;105)
% Mud	73 (65;82)	84 (79;89)	34 (24;47)	14 (5;35)	46 (36;60)	77 (73;81)
TOC (mg/g)	11 (9.2;14)	17 (15;18)	7.3 (6.0;8.9)	4.5 (3.4;6.1)	8.3 (7.0;10)	13 (7.4;25)

[a] All concentrations reported as geometric means with lower and upper 95% confidence limits in parentheses.

FIGURE 6.19 THREE-YEAR MEAN SATURATED HYDROCARBON CONCENTRATIONS, PERCENT MUD, AND TOTAL ORGANIC CARBON IN EAST HARRISON BAY BULK SEDIMENTS.

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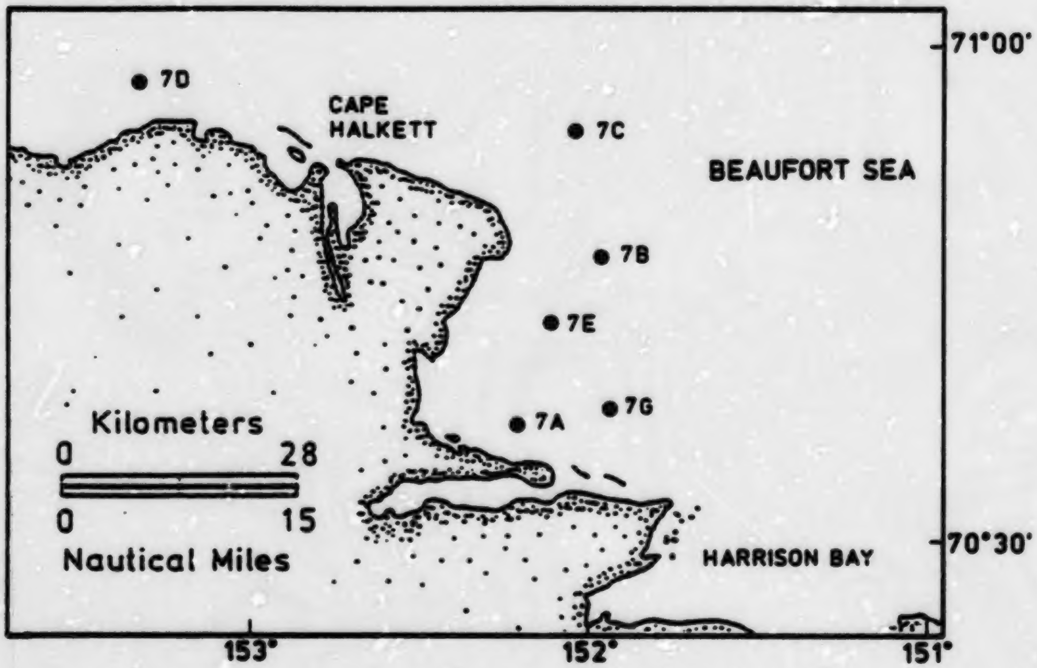

SATURATED HYDROCARBONS (μg/g)[a]	STATIONS					
	7A	7B	7C	7D	7E	7G
TALK	8.4 (4.9;14)	4.2 (2.6;6.7)	9.9 (7.3;13)	5.6 (1.2;27)	9.8 (7.9;12)	5.9 (3.8;9.3)
LALK	1.1 (1.0;1.2)	0.76 (0.45;1.3)	1.5 (1.3;1.8)	0.79 (0.17;3.6)	1.6 (1.4;1.7)	1.1 (0.10;1.3)
Pris	0.09 (0.07;0.12)	0.05 (0.03;0.07)	0.12 (0.09;0.16)	0.07 (0.02;0.26)	0.17 (0.14;0.21)	0.20 (0.19;0.22)
Phyt	0.04 (0.03;0.07)	0.02 (0.01;0.04)	0.06 (0.04;0.07)	0.03 (0.01;0.11)	0.05 (0.04;0.07)	0.05 (0.04;0.06)
TOT	24 (20;28)	11 (6.6;18)	30 (24;37)	25 (13;47)	13 (2.7;63)	21 (18;25)
% Mud	62 (53;71)	12 (7;19)	86 (84;89)	25 (10;62)	69 (62;78)	23 (9;55)
TOC (mg/g)	10 (9.2;11)	5.3 (4.9;5.6)	11 (7.5;16)	6.4 (2.7;15)	17 (12;25)	13 (6.9;25)

[a] All concentrations reported as geometric means with lower and upper 95% confidence limits in parentheses.

FIGURE 6.20 THREE-YEAR MEAN SATURATED HYDROCARBON CONCENTRATIONS, PERCENT MUD, AND TOTAL ORGANIC CARBON IN WEST HARRISON BAY BULK SEDIMENTS.

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Data for East and West Harrison Bay are presented [illegible] Figures 6.19 and 6.20, respectively. The highest sedi[illegible] concentrations of saturated hydrocarbons are associated [illegible] Stations 6A, 6B, and 6G, near the mouth of the Colville [illegible]r. Saturated hydrocarbon concentrations, grain size, and TOC concentrations follow the offshore gradient represented by Stations 6B, 6C, and 6D.

6.3.2 Aromatic Hydrocarbons in Sediments

The aromatic hydrocarbon parameters for the 39 Study Area stations are presented in Figures 6.21 through 6.27. Percent mud and TOC concentrations are included for comparison. Overall, mean aromatic hydrocarbon concentrations followed trends similar to those of the saturated hydrocarbons. The overall highest concentrations of aromatics are found in sediments at Station 6B.

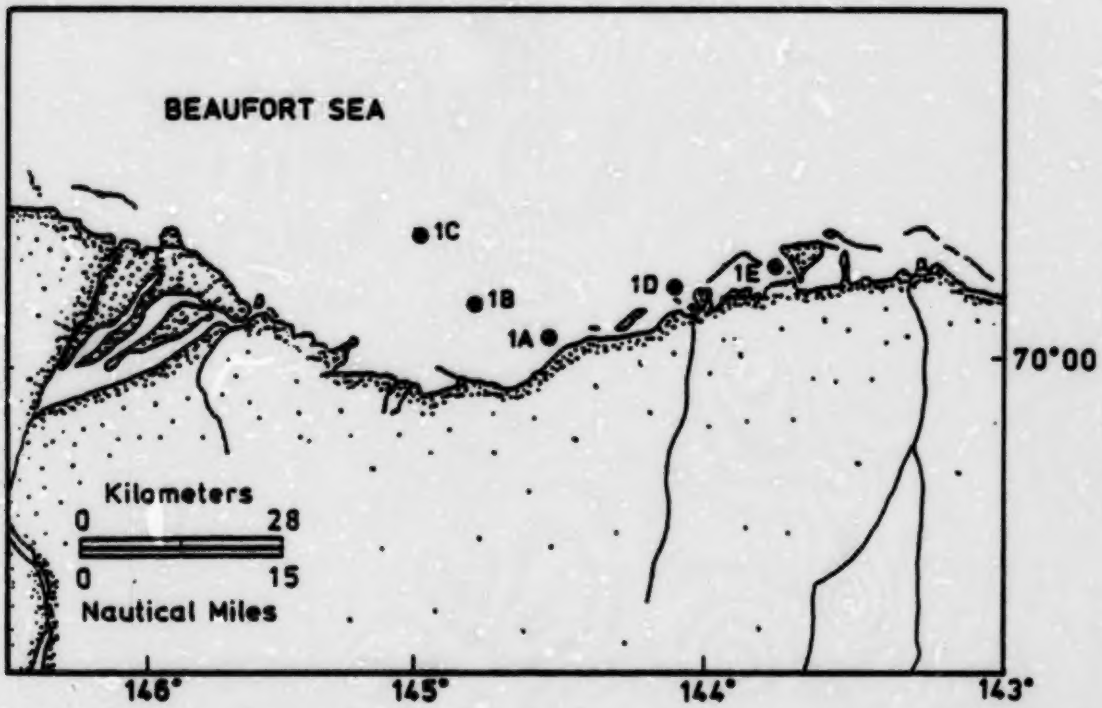
The naphthalene (N) compounds exhibited the widest range in concentrations (0.02-2.0 µg/g). The phenanthrenes (P), dibenzothiophenes (D), and fluorenes (F) range from below detection limits to 0.9, 0.18, and 0.41 µg/g, respectively. The polynuclear aromatic hydrocarbons (PAH) were detected at concentrations between 0.01 and 0.64 µg/g.

Data for the Camden Bay area are presented in Figures 6.21 and 6.22. As was noted with saturated hydrocarbon data, no nearshore-to-offshore gradients were detectable in either the Station 1A, 1B, 1C, or 2A, 2B, 2C transects. The highest aromatic concentrations are associated with the nearshore Station 2A.

Data for the Foggy Island Bay area are presented in Figure 6.23. The trends observed at these stations are similar to trends noted with the saturated hydrocarbon data. Highest concentrations are associated with sediments from Stations 3A, 3B, and 4A; these stations also have relatively high percent mud and TOC concentrations. The lowest concentrations are found at Station 4B. No concentration gradient was associated with the Foggy Island Bay nearshore-to-offshore transect (Stations 4A, 4B, and 4C).

Aromatic hydrocarbon concentrations in the Endicott Field and Kuparuk River area sediments also followed the trends described for the saturated hydrocarbons. With respect to the entire Study Area, sediment aromatics are generally low in the Endicott Field stations. No concentration gradient away from the Endicott Field was observed for the aromatic data. Highest PAH concentrations were observed at the nearshore Station 5D and offshore Stations 5B and 5E.

Aromatic data for the Harrison Bay area are presented in Tables 6.26 and 6.27. The highest sediment aromatic hydrocarbon



AROMATIC HYDROCARBONS (ng/g)[a]	SEDIMENTS 1A	1B	1C	1D	1E
N	0.10 (0.04;0.22)	0.03 (0.03;0.04)	0.17 (0.10;0.27)	0.02 (0.02;0.03)	0.02 (0;0.10)
P	0.09 (0.05;0.15)	0.04 (0.03;0.04)	0.13 (0.08;0.22)	0.02 (0.01;0.03)	0.02 (0.01;0.07)
D	0.01 (0.01;0.02)	0.01 (0.0;0.06)	0.02 (0.0;0.07)	< D.L.[b]	< D.L.
F	0.02 (0.01;0.04)	0.03 (0.0;0.18)	0.04 (0.01;0.14)	< D.L.	< D.L.
PAH	0.09 (0.08;0.11)	0.05 (0.03;0.09)	0.19 (0.13;0.28)	0.01 (0.0;0.04)	0.02 (0.0;0.08)
% Mud	64 (57;72)	13 (11;15)	70 (70;70)	24 (11;51)	50 (14;169)
TOC (mg/g)	9.6 (6.7;14)	7.2 (5.8;9.0)	8.9 (7.8;10)	5.9 (4.7;7.4)	6.8 (2.4;19)

[a] All concentrations reported as geometric means with lower and upper 95% confidence limits in parentheses.

[b] Less than detection limit.

FIGURE 6.21 THREE-YEAR MEAN AROMATIC HYDROCARBON CONCENTRATIONS, PERCENT MUD, AND TOTAL ORGANIC CARBON IN EAST CAMDEN BAY AREA BULK SEDIMENTS.

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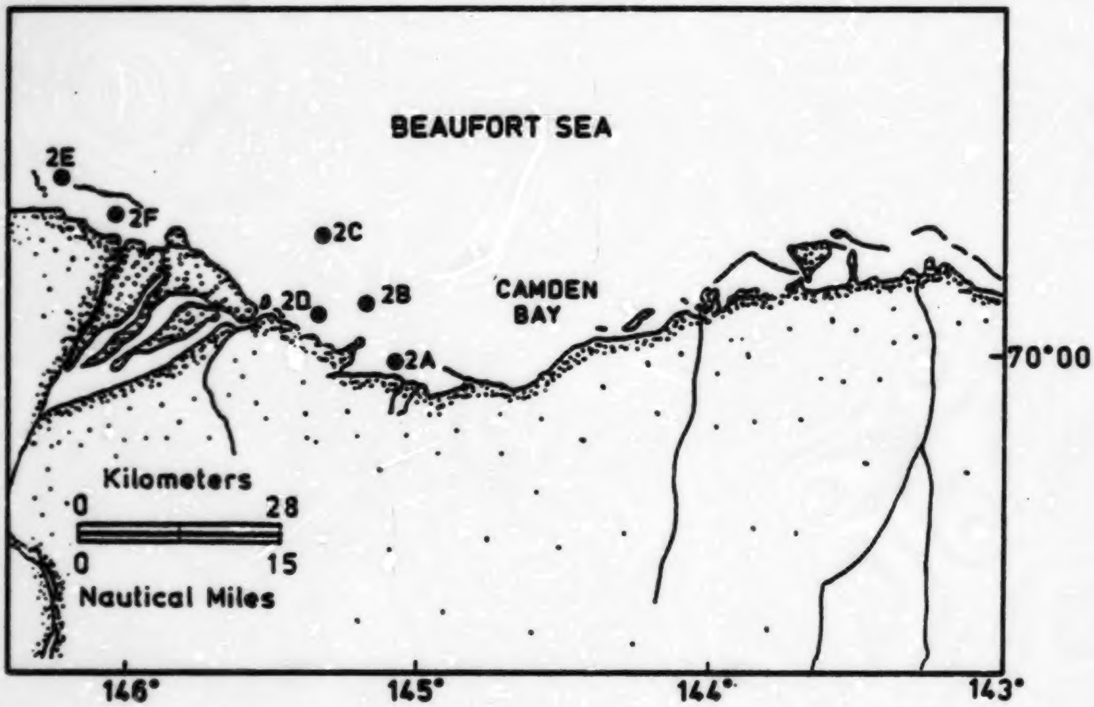

AROMATIC HYDROCARBONS (μg/g)[a]	STATIONS					
	2A	2B	2C	2D	2E	2F
N	0.30 (0.29;0.32)	0.05 (0.04;0.07)	0.28 (0.19;0.42)	0.11 (0.05;0.24)	0.06 (0.02;0.20)	0.03 (0.02;0.05)
P	0.37 (0.36;0.37)	0.05 (0.04;0.07)	0.20 (0.15;0.28)	0.09 (0.03;0.22)	0.07 (0.03;0.16)	0.05 (0.03;0.08)
D	0.05 (0.04;0.06)	0.01 (0.01;0.01)	0.05 (0.03;0.09)	0.02 (0.01;0.03)	0.01 (0.0;0.02)	< D.L.[b]
F	0.10 (0.09;0.10)	0.01 (0.01;0.02)	0.08 (0.06;0.12)	0.03 (0.01;0.04)	0.02 (0.0;0.11)	0.01 (0.01;0.01)
PAH	0.31 (0.30;0.31)	0.05 (0.03;0.09)	0.22 (0.21;0.23)	0.08 (0.07;0.10)	0.05 (0.01;0.18)	0.02 (0.02;0.04)
% Mud	86 (75;98)	10 (9;11)	64 (51;79)	17 (13;23)	27 (7;98)	13 (11;15)
TOC (mg/g)	13 (9.2;19)	5.3 (1.5;18)	8.7 (6.2;12)	7.4 (5.0;11)	5.0 (2.2;12)	4.3 (3.0;6.0)

[a] All concentrations reported as geometric means with lower and upper 95% confidence limits in parentheses.

[b] Less than detection limit.

FIGURE 6.22 THREE-YEAR MEAN AROMATIC HYDROCARBON CONCENTRATIONS, PERCENT MUD, AND TOTAL ORGANIC CARBON IN WEST CAMDEN BAY AREA BULK SEDIMENTS.

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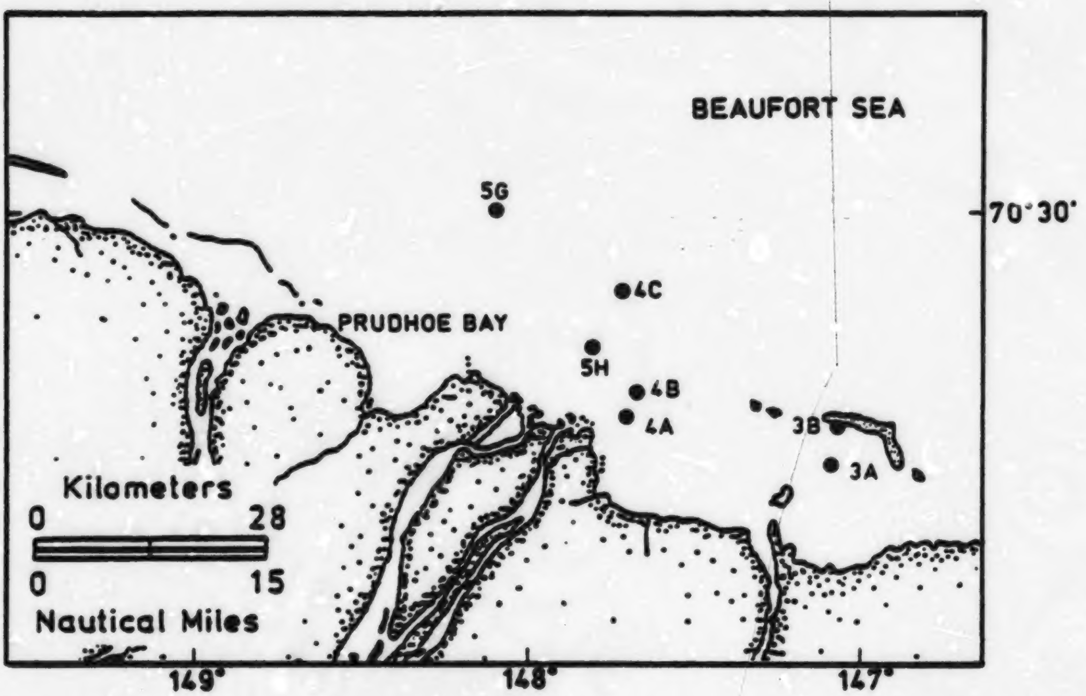

AROMATIC HYDROCARBONS (µg/g)[a]				STATIONS			
	3A	3B	4A	4B	4C	5G	5H
N	0.13 (0.11;0.16)	0.13 (0.09;0.19)	0.12 (0.09;0.17)	0.05 (0.03;0.08)	0.07 (0.06;0.09)	0.08 (0.06;0.13)	0.05 (0.04;0.07)
P	0.13 (0.09;0.18)	0.15 (0.14;0.17)	0.12 (0.07;0.19)	0.04 (0.04;0.05)	0.07 (0.06;0.10)	0.07 (0.04;0.13)	0.06 (0.05;0.07)
D	0.02 (0.01;0.03)	0.02 (0.02;0.03)	0.02 (0.01;0.06)	0.01 (0.0;0.02)	0.01 (0.01;0.02)	0.01 (0.0;0.02)	0.02 (0.02;0.03)
F	0.03 (0.03;0.04)	0.03 (0.02;0.04)	0.02 (0.01;0.07)	0.01 (0.01;0.02)	0.02 (0.02;0.02)	0.01 (0.01;0.02)	0.03 (0.02;0.04)
PAH	0.09 (0.09;0.10)	0.09 (0.07;0.11)	0.07 (0.04;0.11)	0.03 (0.02;0,06)	0.06 (0.05;0,08)	0.07 (0.06;0.09)	0.05 (0.04;0.07)
% Mud	38 (28;51)	69 (64;74)	30 (27;33)	8 (5;12)	11 (6;20)	15 (11;22)	18 (13;24)
TOC (mg/g)	8.6 (6.8;11)	10 (9.1;11)	7.8 (4.4;13)	3.4 (2.5;4.5)	4.9 (2.2;11)	5.6 (4.4;7.2)	9.2 (4.4;19)

[a] All concentrations reported as geometric means with lower and upper 95% confidence limits in parentheses.

FIGURE 6.23 THREE-YEAR MEAN AROMATIC HYDROCARBON CONCENTRATIONS, PERCENT MUD, AND TOTAL ORGANIC CARBON IN FOGGY ISLAND BAY AREA BULK SEDIMENTS.

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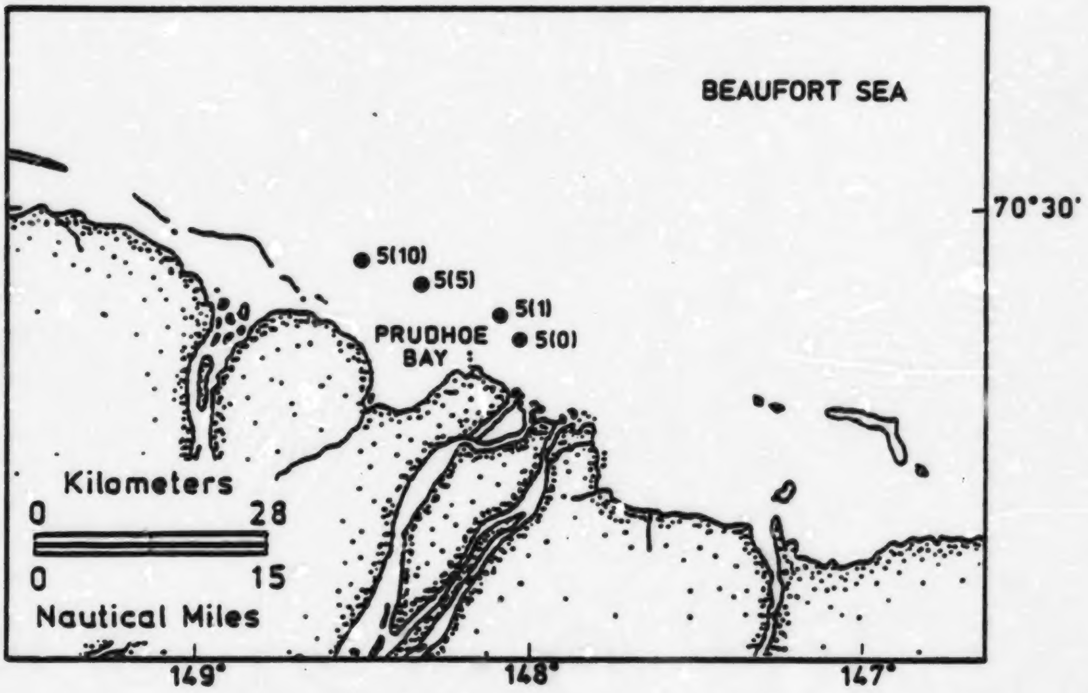

AROMATIC HYDROCARBONS (ug/g)[a]	STATIONS			
	5(0)	5(1)	5(5)	5(10)
N	0.04 (0.02;0.09)	0.03 (0.02;0.05)	0.06 (0.02;0.18)	0.08 (0.04;0.14)
P	0.03 (0.02;0.06)	0.03 (0.02;0.06)	0.07 (0.03;0.19)	0.08 (0.04;0.16)
D	0.01 (0.0;0.2)	0.01 (0.0;0.2)	0.01 (0.0;0.04)	0.02 (0.01;0.03)
F	0.01 (0.01;0.02)	0.01 (0.0;0.01)	0.02 (0.01;0.04)	0.02 (0.01;0.05)
PAH	0.03 (0.03;0.03)	0.03 (0.02;0.04)	0.05 (0.02;0.13)	0.06 (0.05;0.08)
% Mud	7 (3;13)	3 (1;12)	21 (11;39)	22 (15;33)
TOC (mg/g)	3.4 (2.5;4.5)	3.5 (2.5;4.9)	5.7 (3.6;8.9)	7.2 (4.8;11)

[a] All concentrations reported as geometric means with lower and upper 95% confidence limits in parentheses.

FIGURE 6.24 THREE-YEAR MEAN AROMATIC HYDROCARBON CONCENTRATIONS, PERCENT MUD, AND TOTAL ORGANIC CARBON IN ENDICOTT FIELD BULK SEDIMENTS.

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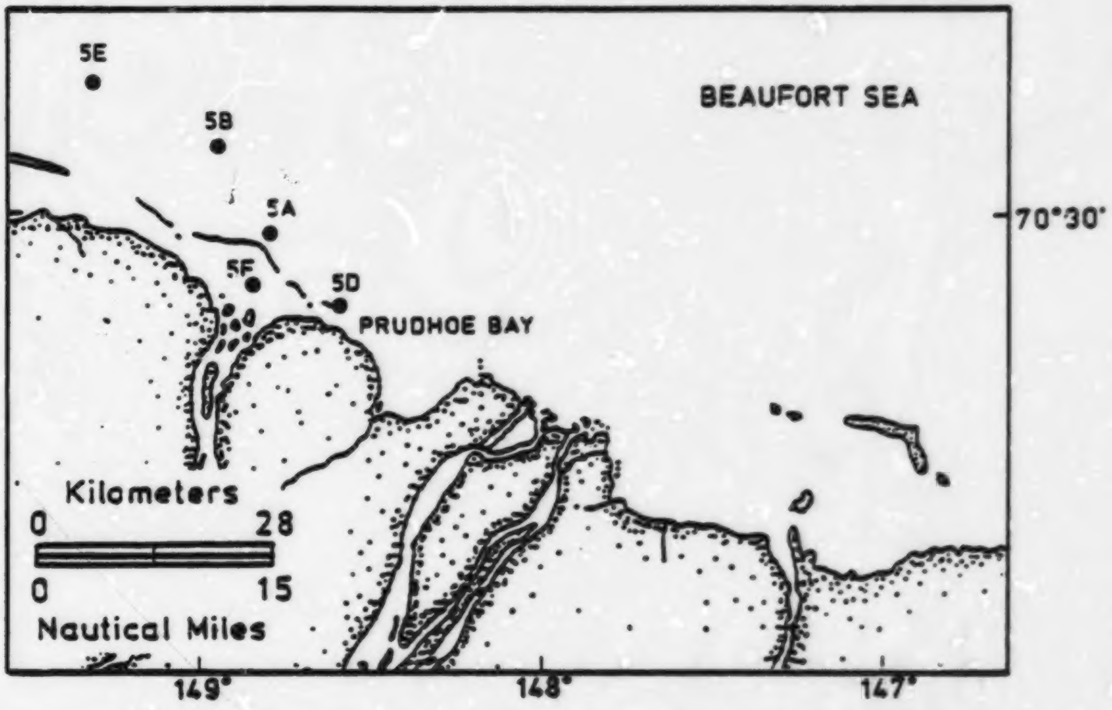

AROMATIC HYDROCARBONS (μg/g)[a]	STATIONS				
	5A	5B	5D	5E	5F
N	0.21 (0.15;0.29)	0.32 (0.21;0.49)	0.27 (0.19;0.37)	0.28 (0.15;0.50)	0.14 (0.06;0.31)
P	0.14 (0.08;0.26)	0.27 (0.21;0.35)	0.22 (0.12;0.39)	0.42 (0.17;0.33)	0.12 (0.05;0.27)
D	0.02 (0.02;0.03)	0.06 (0.06;0.07)	0.05 (0.03;0.07)	0.05 (0.04;0.06)	0.03 (0.02;0.05)
F	0.03 (0.02;0.04)	0.08 (0.07;0.11)	0.04 (0.04;0.05)	0.05 (0.04;0.08)	0.02 (0.01;0.06)
PAH	0.13 (0.10;0.16)	0.18 (0.08;0.37)	0.17 (0.13;0.23)	0.17 (0.08;0.38)	0.13 (0.06;0.26)
% Mud	53 (39;72)	22 (3;148)	68 (61;74)	25 (12;55)	52 (42;64)
TOC (mg/g)	9.6 (6.3;14)	5.2 (2.0;13)	18 (11;29)	8.1 (5.9;11)	12 (7.3;18)

[a] All concentrations reported as geometric means with lower and upper 95% confidence limits in parentheses.

FIGURE 6.25 THREE-YEAR MEAN AROMATIC HYDROCARBON CONCENTRATIONS, PERCENT MUD, AND TOTAL ORGANIC CARBON IN THE KUPARUK RIVER AREA BULK SEDIMENTS.

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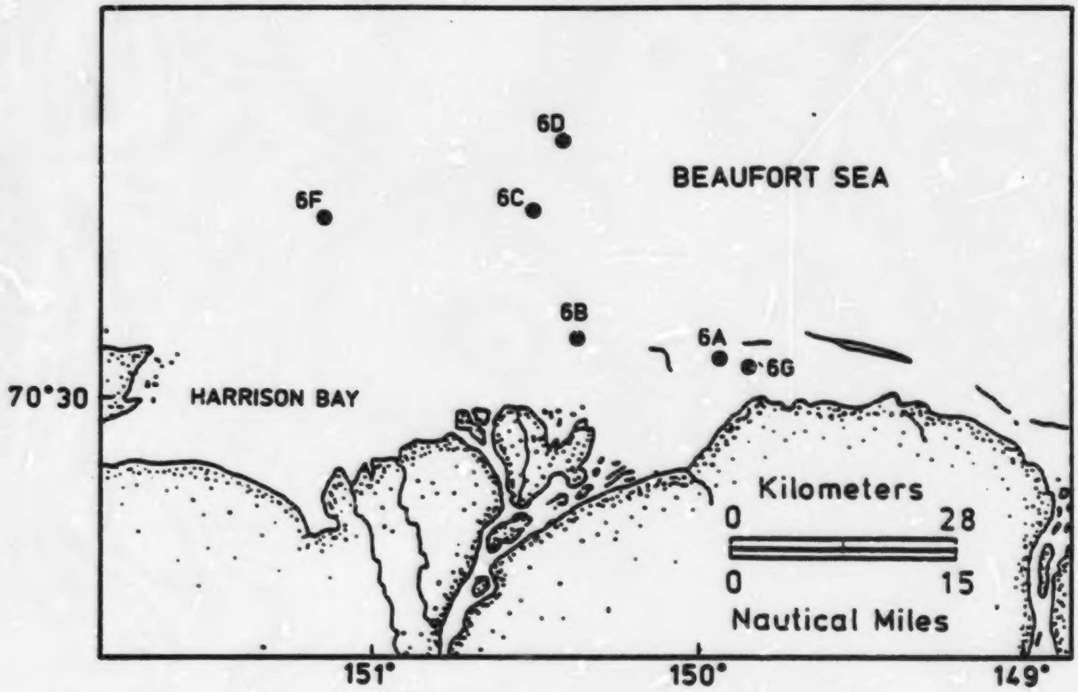

AROMATIC HYDROCARBONS (µg/g)[a]	STATIONS					
	6A	6B	6C	6D	6F	6G
N	0.45 (0.41;0.50)	2.0 (0.99;3.9)	0.32 (0.28;0.37)	0.14 (0.06;0.33)	0.32 (0.21;0.49)	0.35 (0.18;0.66)
P	0.31 (0.23;0.40)	0.90 (0.38;2.1)	0.25 (0.18;0.34)	0.10 (0.06;0.18)	0.22 (0.11;0.41)	0.21 (0.12;0.36)
D	0.08 (0.05;0.13)	0.18 (0.08;0.37)	0.05 (0.04;0.08)	0.02 (0.01;0.04)	0.04 (0.02;0.08)	0.04 (0.03;0.06)
F	0.12 (0.09;0.15)	0.41 (0.22;0.76)	0.07 (0.04;0.12)	0.03 (0.01;0.08)	0.08 (0.06;0.12)	0.07 (0.05;0.10)
PAH	0.21 (0.13;0.33)	0.64 (0.32;1.3)	0.19 (0.16;0.23)	0.08 (0.05;0.13)	0.16 (0.09;0.27)	0.16 (0.07;0.39)
% Mud	73 (65;82)	84 (79;89)	34 (24;47)	14 (5;35)	46 (36;60)	77 (73;81)
TOC (mg/g)	11 (9.2;14)	17 (15;18)	7.3 (6.0;8.9)	4.5 (3.4;6.1)	8.3 (7.0;10)	13 (7.4;25)

[a] All concentrations reported as geometric means with lower and upper 95% confidence limits in parentheses.

FIGURE 6.26 THREE-YEAR MEAN AROMATIC HYDROCARBON CONCENTRATIONS, PERCENT MUD, AND TOTAL ORGANIC CARBON IN EAST HARRISON BAY BULK SEDIMENTS.

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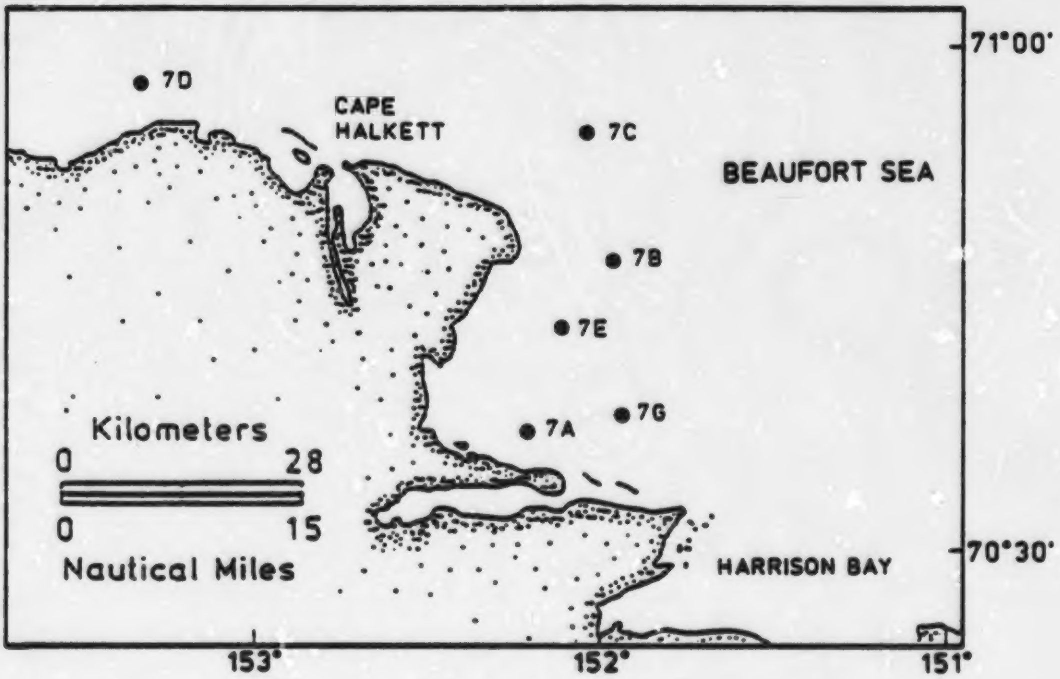

AROMATIC HYDROCARBONS (µg/g)[a]	STATIONS 7A	7B	7C	7D	7E	7G
N	0.49 (0.42;0.57)	0.18 (0.11;0.29)	0.66 (0.63;0.70)	0.17 (0.07;0.41)	0.82 (0.73;0.93)	0.56 (0.28;1.2)
P	0.28 (0.19;0.42)	0.12 (0.07;0.21)	0.46 (0.35;0.61)	0.15 (0.03;0.62)	0.41 (0.33;0.50)	0.37 (0.26;0.53)
D	0.07 (0.04;0.12)	0.03 (0.01;0.05)	0.10 (0.09;0.11)	0.03 (0.01;0.10)	0.07 (0.06;0.10)	0.05 (0.04;0.05)
F	0.11 (0.07;0.19)	0.03 (0.02;0.06)	0.12 (0.09;0.16)	0.03 (0.01;0.15)	0.09 (0.07;0.12)	0.03 (0.01;0.08)
[illegible]	0.18 (0.13;0.25)	0.10 (0.06;0.16)	0.21 (0.08;0.52)	0.11 (0.05;0.24)	0.27 (0.24;0.31)	0.20 (0.17;0.24)
% Mud	62 (53;71)	12 (7;19)	86 (84;89)	25 (10;62)	69 (62;78)	23 (9;55)
TOC (mg/g)	10 (9.2;11)	5.3 (4.9;5.6)	11 (7.5;16)	6.4 (2.7;15)	17 (12;25)	13 (6.9;25)

[a] All concentrations reported as geometric means with lower and upper 95% confidence limits in parentheses.

FIGURE 6.27 THREE-YEAR MEAN AROMATIC HYDROCARBON CONCENTRATIONS, PERCENT MUD, AND TOTAL ORGANIC CARBON IN WEST HARRISON BAY BULK SEDIMENTS.

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concentrations, not only in this region, but also in the entire Study Area, are clearly associated with Station 6B, located near the mouth of the Colville River. As was noted with the saturated hydrocarbon data, an offshore concentration gradient is clearly indicated in the 6B, 6C, 6D transect, with lowest values occurring at Station 6D. In West Harrison Bay (Figure 6.27), highest aromatic hydrocarbon concentrations were found at Stations 7C and 7E. The lowest levels of all parameters occurred in Station 7B sediments.

6.4 QUALITY CONTROL RESULTS

This section summarizes the results of the three-year analytical quality control (QC) measures employed in the analysis of trace metals and hydrocarbons. All data are presented in tabular form in Appendix B.

6.4.1 Trace Metals

QC measures for the trace metals analyses during the three years of the program included determinations of analytical accuracy and precision, replicate procedural blanks and reagent blanks, and analysis of metals by more than one technique.

During the entire program, accuracy was determined by analysis of Standard Reference Material (SRM) sediment standards MESS-1 and NBS-1646 (Year-2 only), and oyster tissue standard NBS-1566. Results of replicate analyses of these standards and the certified, or best, value are presented in Appendix B, Tables B.1 through B.7. Generally, the range of values obtained overlaps the range of best values, verifying that the methods employed were accurate.

Analytical precision was also determined by analysis of the SRM (Tables B.1 through B.7). The precision (coefficient of variation, CV) for metals in sediment is 10 percent or less. With the exception of chromium which showed greater variability, the precision is also excellent for tissue samples.

Detection limits were calculated from the procedural blanks by using twice the standard deviation of the mean for replicate procedural blanks (Tables B.8 through B.13). The detection limits were mostly in the range of one-tenth to several ppm dry weight. Reagent blanks were determined prior to analysis of the field samples to verify that the detection limits would not be adversely affected by reagents. Data for these analyses are given in Tables B.14 through B.19 for sediments and tissues, respectively.

Approximately 10 percent of the sediment samples were analyzed by both XRF and ICAP. The XRF technique does not require sediment dissolution. Comparisons of the data obtained by the two techniques are shown in Tables B.20 through B.22. The means of triplicate field grab samples are usually within two standard deviations for the different techniques.

6.4.2 Hydrocarbons

QC for the hydrocarbon program included initial and ongoing determinations of analytical precision and accuracy through the analysis of SRMs, method blanks, spiked blank samples, matrix spike samples, and the reextraction of samples.

6.4.2.1 Standard Reference Materials

During Year-1 of the survey, the laboratory analyzed National Oceanic and Atmospheric Administration/National Analytical Facility (NOAA/NAF) reference sediment samples. These data are shown in Table B.23. Because the values determined by the NOAA/NAF were not known, we were unable to comment on the agreement of our data with those of NOAA laboratories. However, it is evident from Table B.23 that excellent agreement was attained among the three replicates analyzed, indicating good analytical precision. A similar conclusion can be derived from the sample concentrations of individual n-alkanes (Table B.24) and PAHs (Table B.25). Because no SRM was included in these analyses, a determination of accuracy could not be made in this sample set.

Before analysis of the field sampling in Year-2, the laboratory participated in a laboratory intercalibration exercise consisting of triplicate analyses of interim reference sediments and mussel homogenate. The intercalibration was administered by National Oceanic and Atmospheric Administration, National Marine Fisheries Service (NOAA/NMF) Laboratory in Seattle, WA.

Results of Battelle participation in this exercise are shown in Tables B.26 through B.29. A comparative set of reference data for relatively few analytes (PAH only) is presented in Table B.30. A direct comparison of the parent aromatic hydrocarbon compounds reveals that, although preparation and analysis methods differed considerably from those employed by NOAA, the concentrations of PAHs detected by Battelle are virtually identical to PAH levels reported by the participating NOAA laboratories. For PAH analysis, NOAA laboratories utilized GC-FID, a technique that necessitates size-exclusion chromatography for the preparation of sample extracts prior to analysis. This method is useful for the identification of parent 2- to 5-ring aromatic compounds. However, for programs such as the BSMP, this type of data set is too limited for detailed geochemical characterization of the sediment and for determination of petroleum-related additions to sediments and tissues.

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During Year-3 of the program, Canadian Test Sediment HS-2 from the National Research Council of Canada was analyzed by GC-FID and GC/MS. The data are presented in Tables B.31 and B.32 of Appendix B.

6.4.2.2 Ongoing Quality Control

Ongoing determinations of precision and accuracy were carried out through the analysis of method blanks, spiked blanks, and triplicate analyses of spiked samples. Method blank samples were analyzed along with every batch of sediment and tissues processed in the laboratory. A batch of sediment (including peat and mud fractions) generally consisted of 9 to 12 field samples plus the appropriate QC samples. A batch of tissue samples usually included four to six field samples plus the QC samples.

6.4.2.2.1 Method Blanks. During Year-1 of the program, method blanks analyzed by UV/F at 312 and 355 nm emission wavelength yielded total laboratory background concentrations between 0 and 35.6 µg Prudhoe Bay crude oil equivalent which, when divided by a sample weight (e.g., 150 g of sediment) are within an acceptable range. Some of the background at 312 nm may be due to the o-terphenyl internal standard. The same blanks analyzed by GC-FID showed a series of small peaks (probably phthalic acid esters) eluting around n-C25. Potential interferences from these components were considered minimal.

The results of Year-2 method blank analyses are presented in Tables B.33 through B.35. Sediment samples ranged in weight from 53 to 113 g dry weight, generally exceeding 80 g. The method blank data are normalized to 50 g dry weight for direct comparison with the survey data. The wet weight of tissue samples ranged from 3.6 to 15.3 g and generally exceeded 10 g. Tissue blank data are normalized to 10 g wet weight for direct comparison to the survey data. Method detection limits (MDL) determined by the instrument calibration range for the above sample sizes for individual n-alkanes are 0.0002 µg/g dry weight and 0.0010 µg/g wet weight for sediment and tissue, respectively. Corresponding MDL for individual PAH are the same. Hydrocarbon concentrations less than 0.001 µg/g are not reported.

Year-2 method blanks analyzed by GC-FID revealed hydrocarbon concentrations ranging from 0.06 to 0.60 µg/g dry weight and 0.1 to 1.3 µg/g wet weight for sediment and tissue analyses, respectively. The same samples analyzed by GC/MS revealed total PAH concentrations ranging from less than detection limit to 0.064 µg/g dry weight and from 0.001 to 0.041 µg/g wet weight for sediments and tissues, respectively. Except for tissue PAH, all method blanks represented less than 10 percent of the total hydrocarbons (saturates or aromatics) found in the samples accompanying the blanks. Because many tissue PAH levels are extremely low, approaching MDL, levels found in these samples are similar to those found in the blanks. However, tissue PAH levels are reported uncorrected for laboratory background. Analysis of method blanks by GC-FID revealed the presence of small peaks eluting with undecane (n-C11) and near pentacosane (n-C25). The potential interferences from peaks at n-C25 were considered minimal. All field samples were reviewed for the presence of contamination at n-C11 and corrections made, if necessary, in the calculation of the hydrocarbon parameters containing this peak. PAHs generally present in procedural blanks included naphthalene, phenanthrene, and perylene. However, the concentrations of these compounds were generally low and not considered as interfering in the analysis of any field samples except those tissue samples exhibiting the lowest PAH levels. Tissue samples were additionally analyzed by UV/F spectroscopy. The concentrations of hydrocarbons quantified as Prudhoe Bay crude oil equivalents range from less than detection limit to 0.55 μg/g wet weight. Background oil concentrations generally increased with decreasing wavelength.

Year-3 method blank data are presented in Tables B.36 through B.38 of Appendix B. The method blank data are normalized to 50 g dry weight for sediment samples. The tissue data are normalized to 10 g dry weight. The MDL are the same as in Year-2 of the program.

Year-3 method blanks analyzed by GC-FID revealed hydrocarbon concentrations ranging from less than the detection limit to 0.48 μg/g dry weight and 0.2 to 12.8 μg/g wet weight for sediment and tissue analysis, respectively. However, samples processed with tissue method blank and with a hydrocarbon concentration of 12.8 μg/g dry weight were reanalyzed, and the hydrocarbon contamination was determined to be isolated in the procedural blank. Most tissue blank hydrocarbon concentrations ranged between 0.2 and 0.6 μg/g wet weight.

The same method blanks analyzed by GC/MS revealed total PAH concentrations ranging from less than the detection limit to 0.003 μg/g dry weight and less than the detection limit to 0.048 μg/g wet weight for sediments and tissues, respectively.

Year-3 tissue method blanks were also analyzed by UV/F spectroscopy. The hydrocarbon concentrations quantified as Prudhoe Bay crude oil equivalents ranged from less than the detection limit to 0.89 μg/g wet weight.

6.4.2.2.2 Additional Quality Control Measure for Year-1. Year-1 blank spikes consisted of a mixture of n-alkanes (range n-C10 to n-C34) and a 1-mL ampoule of NBS-SRM 1647 (PAH in acetonitrile). Recoveries of the n-alkanes, calculated versus added internal standard (androstane) ranged between 50 and 100 percent, with lower recoveries associated with the more volatile components. Recoveries of individual PAH in NBS-SRM 1647 are listed in Appendix-B Table B.39. Recoveries of several PAH were low and somewhat variable. Steps were taken, prior to the Year-2 and Year-3 analyses, to modify analytical procedures (in particular, solvent concentration methods which represent a major source of volatilization losses) to gain higher and more uniform PAH recoveries.

To determine the adequacy of the extraction methods, sediment samples were reextracted during Year-1, and found to contain between 0.01 and 0.09 μg/g dry weight total saturated hydrocarbons, indicating that the extraction method employed thoroughly extracted all hydrocarbons.

Four additional sediments were fortified with Prudhoe Bay crude oil following initial extraction in Year-1, then reextracted and analyzed by UV/F to determine total oil concentrations. The results, shown in Table B.40 of Appendix B, indicate recovery of the spike ranges between 60 to 75 percent.

6.4.2.2.3 Additional Quality Control Measures for Year-2.

During Year-2, a series of procedural spiked blanks was processed and analyzed along with the sediment and peat samples. The results of these analyses are presented in Tables B.41 and B.42. Recoveries of the analytes spiked in the first four samples analyzed by GC-FID and in the first three samples analyzed by GC/MS were low. Upon investigation, it was determined that these samples, because of the lack of an extract "matrix", tended to evaporate to dryness during the routine concentration procedure. Careful observation of the sample extracts during the concentration steps remedied this problem and subsequent analyses produced acceptable recoveries. Analysis of the spiked blank samples by GC-FID also revealed the presence of a contaminant coeluting with n-C11. Recoveries, presented in Appendix-B Tables B.41 and B.42, represent absolute recoveries of analytes determined by a quantification standard placed in the sample immediately before analysis. Field sample analyte concentrations are calculated against an internal standard placed in the sample before analysis and, thus, reported concentrations are always corrected for recovery.

Precision was determined by the analysis of triplicate sediment and tissue samples (UV/F only) spiked with Prudhoe Bay crude oil (Appendix-B Tables B.43 and B.44), and the analysis of triplicate tissue homogenates (Table B.45) in Year-2. Results of the sediment analyses indicate very tight analytical precision for the gravimetric data (CV <1.5), but somewhat less precise chromatographic data. The least precise measurement was the GC-FID calculation of UCM (CV $= 35.6$). Analysis of the tissue triplicate experiments revealed much higher precision with the spiked sample than with the sample containing hydrocarbons at arctic background concentrations. Recoveries of oil in the spiked tissue samples were 92 percent and 79 percent at 312 nm and 425 nm, respectively. Recovery data for the spiked sediment experiment is more difficult to interpret because no analysis of the crude extract was performed. Total saturated and aromatic hydrocarbon weight was 54 percent of the amount of crude oil spiked into the sample.

6.4.2.2.4 Additional Quality Control Measures for Year-3. Year-3 spiked method blanks data are presented in Appendix-B Tables B.46 and B.47 for GC-FID and GC/MS analyses, respectively. The recoveries reported are recoveries of analytes determined by a quantification standard placed in the sample prior to extraction. Recoveries ranged between 100 and 202 percent and 85 to 136 percent for GC-FID and GC/MS analyses, respectively.

6.4.3 Total Organic Carbon

Table B.48 in Appendix B presents the results of the Year-1 QC data obtained for the total organic carbon analyses. Single replicate samples from two stations were randomly chosen and split. Three analyses were performed on each sample to determine reproducibility of the analytical method. As can be noted from the data, variability between splits is minimal and indicates acceptable analytical precision. Because no SRM or spiked samples were analyzed, accuracy could not be determined.

The QC program for total organic carbon analyses continued through Year-2 and Year-3. The carbon analyzer was calibrated daily with a series of calibration standards to provide a calibration curve covering the range of interest.

6.4.4 Grain Size

The quality control program maintained by the sediment grain size laboratory is part of a Battelle laboratory-wide QA/QC program. Measures included documentation of sample handling, and the analysis of reagent QC checks and split samples to ascertain method variability.

Table B.49 in Appendix B presents Year-1 results of nine duplicate sediment grain-size analyses performed during the course of the analytical work. Approximately 10 percent of both the Year-2 and Year-3 field samples were split and analyzed as duplicates. Results of these analyses are presented in Tables B.50 and B.51. These data indicate that, for the wide range of sediment textures analyzed, reproducibility of the methods employed is acceptable. As can be expected, the greatest variability is observed in the -1 phi category (gravel). Comparison of the results in other phi classes indicates very good analytical precision. Because no SRM was included in the analyses, a determination of accuracy could not be made in these sample sets.

7.0 ANALYSIS AND INTERPRETATION OF DATA

7.1 INTRODUCTION

The analysis of the three-year data set includes the same approaches as were used in interpreting the data in the previous Annual Reports (Boehm et al., 1985; 1986). These approaches include the following:

1. Evaluation of the data from geochemical and biogeochemical perspectives.
2. Statistical analysis of the data to test hypotheses.

7.1.1 Geochemical and Biogeochemical Evaluation

The first approach concerns the interpretation of the spatial aspects of the data with regard to both the concentrations of target metallic elements and organic compounds, and the compositional aspects of the data. Included are the evaluations of key diagnostic parameters and parameter ratios. In this evaluation, special attention is given to associations between chemical distributions in sediments and their possible sources. Coastal peat and riverine inputs of particulate materials and their associated assemblages of metals and organics are discussed in relation to the observed distribution of chemicals in offshore sediment. In the context of evaluating the data for their relevance to monitoring possible contributions from oil and gas exploration and production, the importance of background inputs of peat and rivers must be investigated.

The first approach also evaluates the association of the metals and organics with the mud fraction of the sediment. This line of investigation was introduced to the Year-2 program.

Data from the analyses of benthic animals (i.e., bivalve molluscs and selected crustaceans were also evaluated, both from the aspect of chemical content and composition, and with regard to the relationship of tissue chemical levels to those chemical concentrations and compositions in the surrounding sediment. An extensive collection of animals was made and chemically analyzed in the Year-2 and Year-3 program to examine the usefulness of applying the sentinel organism approach to the BSMP.

7.1.2 Statistical Analysis

The second interpretive approach (Section 8) centered on the statistical analyses of the data. This approach included the first opportunity to test the basic hypotheses upon which the monitoring program is based, to evaluate temporal changes in chemical concentrations and in key diagnostic parameters.

In addition to examining the chemical concentrations of the sediments at each station, the Beaufort Sea Study Area was divided into six geographic regions. Each region was composed of stations from one or more similarly numbered station groups (see Figure 4.1):

Region 1 (Camden Bay): 1A, 1B, 1C, 1D, 1E, 2A, 2D, 2C, 2D, 2E, 2F

Region 2 (Foggy Island Bay): 3A, 3B, 4A, 4B, 4C, 5G, 5H

Region 3 (Kuparuk River Bay Area): 5A, 5B, 5D, 5E, 5F

Region 4 (East Harrison Bay): 6A, 6B, 6C, 6D, 6F, 6G

Region 5 (West Harrison Bay): 7A, 7B, 7C, 7D, 7E, 7G

Region 6 (Endicott Field): 5(0), 5(1), 5(5), 5(10)

7.2 TRACE METAL CHEMISTRY

7.2.1 Review of Historical Data

The concentrations of several metals (iron, manganese, copper, cobalt, chromium, nickel, vanadium, and zinc) were determined by Naidu et al. (1981) in several depositional regions (Harrison Bay, Simpson and Beaufort Lagoons) of the Beaufort Sea OCS. Concentrations of all metals in OCS sediments were greater than those found in the nearshore or the coastal lagoons. Total metal concentrations in sediments of the arctic lagoons were comparable to those of nonpolluted temperate sediments. Neither vanadium nor nickel, metals that might indicate petroleum contamination, exhibited a regional distribution consistent with localized petrogenic inputs.

Northern Technical Services (1981, 1982, 1983) reported concentrations of several metals in surficial sediments in the vicinity of exploratory wells at Reindeer Island, the Sag delta, Challenge Island, and Tern Island in state waters of the Beaufort Sea. Before drilling began, sediment concentrations of barium, a major ingredient of drilling muds, ranged from 135 to 4,200 ppm. Highest concentrations were observed in sediments from Challenge Island. Concentrations of chromium, another drilling mud ingredient, ranged from 4 to 110 ppm. Concentrations of nickel and vanadium in sediments ranged from 30 to 50 and 55 to 155 ppm, respectively. Other studies of metal distributions in OCS sediments of the Beaufort Sea have been conducted by Sweeney (1984) and Robertson and Abel (1979).

The concentrations of metals found in bulk sediments in Year-1 and Year-2 of the BSMP are generally similar to values reported by Robertson and Abel (1979) and Naidu et al. (1982) for the Beaufort Sea, and by Campbell and Loring (1980) for Baffin Bay in the Canadian Arctic. As shown in Table 7.1, there are considerable ranges in trace metal concentrations due to both variation in sediment texture and possible differences in analytical techniques. The metal concentrations in Beaufort Sea sediments are in the range of those reported for similarly textured sediments on both the East and West Coasts of the United States (Bothner et al., 1983; Katz and Kaplan, 1981), and are compatible with values for average continental crust (Bowen, 1979)

Northern Technical Services (1981) reported concentrations of cadmium, chromium, lead, and zinc in tissues of Beaufort Sea amphipods (Onisimus sp. and Boeckosimus sp.) to be 0.3, 3.0, 9.7, and 85.8 ppm dry weight, respectively. Northern Technical Services (1982) also measured the concentrations of several metals in the tissues of isopods (Saduria entomon) before and after exploratory drilling off the Sag River delta and at Challenge Island. Concentrations of barium in gutted isopods from the Sag River delta, collected before drilling began, ranged from 110 to 320 ppm, and barium concentrations did not increase in the isopod tissues after drilling. Before drilling began, mean concentrations of cadmium, chromium, copper, lead and zinc in gutted isopod tissues from off the Sag River delta were 1.61, 3.0, 36.0, 10.5, and 61.0 ppm, respectively.

7.2.2 Trace Metal Composition of Sediments

The three-year data set for trace metals in Beaufort Sea sediments reveals a wide range of concentrations (Table 7.1). Levels of trace metals are generally higher in the fine-grained and TOC-enriched sediments collected offshore than in the nearshore, shallow water, sandy Beaufort Sea sediments. Annual variations in the concentrations of metals at a station were generally small, unless significant change in sediment grain size was also noted.

Regional trends in the concentrations of barium and chromium in sediments appear to be caused by local riverine inputs to the Study Area, rather than shoreline erosion of peat deposits. There is no evidence that oil and gas exploration and production activities have resulted in trace metal contamination of the sediments collected at stations in the Beaufort Sea Study Area.

7.2.2.1 Year-to-Year Comparisons of Sediment Trace Metals

During Year-1 and Year-2, bulk sediment samples (without size separation) were analyzed for trace metals. The mud fraction (particles less than 62 μ in diameter) was additionally

TABLE 7.1 RANGE OF TOTAL METAL CONCENTRATIONS IN ARCTIC COASTAL SEDIMENTS COMPARED TO AVERAGE CONTINENTAL CRUST.

METALS (ug/g)[a]	BSMP 3-YR MEANS	NAIDU ET AL., 1982	CAMPBELL & LORING 1980	AVERAGE CONTINENTAL CRUST (BOWEN,1979)
Ba	185-745	-	-	500
Cd	0.04-0.31	-	-	0.11
Cr	17-91	82-97	16-139	100
Cu	4.9-37	0-61	4-42	50
Pb	3.9-20	-	4-42	14
V	33-153	25-275	47-156	160
Zn	19-116	38-130	17-83	75

[a] Dry weight

Dashes indicate no data

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analyzed in the Year-2 program. Only the mud fraction of sediments collected in Year-3 was analyzed for trace metals.

Generally, the concentrations of metals and percent mud in Year-2 bulk sediments were similar to those in Year-1 bulk sediments. For the few stations at which metals differed significantly between years, the percent mud usually differed in a corresponding manner. This was the case for Stations 2E, 5B, and 5E, where metals and percent mud appeared to increase from Year-1 to Year-2. At Station 5A, 5F, and 6F, metals and percent mud both decreased. These results indicate that there were significant annual changes in the grain size and trace metal concentrations at some stations. These annual changes may be due either to sediment transport processes or to within-station inhomogeneity. However, given the precision of station repositioning, the former explanation is more likely. The most dramatic changes were observed at Station 5B, where percent mud increased from 3 to 77 percent and at Station 2E, where mud increased from 8 to 78 percent.

The Year-2 and Year-3 mean log concentrations of metals in the fine sediment fraction, and corresponding TOC and percent mud for the bulk sediments are displayed schematically by region (as defined above) in Figures C.1 through C.9 in Appendix C. In general, little change occurred within a region during a year. When large annual differences occur, they are usually correlated with change in grain size at one or more stations within the region. As an example, the mean log (ln) barium concentrations for Year-2 and Year-3 in fine sediments from six regions are presented in Figure 7.1. The barium concentrations were higher in Year-2 than in Year-3 for Regions 1 and 5, but lower for Region 3 in Year-2 than in Year-3. The statistical significance of these annual differences is discussed in Section 8.

7.2.2.2 Geographic Trends

Metal concentrations in the mud fraction of sediments collected in Year-2 and Year-3 indicate no strong geographic trends (Table 7.2). The Year-1 data also show no geographical trends, other than those attributable to regional differences in grain size and TOC.

The geometric mean concentrations of metals in mud samples collected in Year-2 and Year-3 from six regions of the Beaufort Sea are presented in Table 7.2. Each regional mean was calculated using four to nine station means. Overall, very few regional differences were observed and sediment concentrations are close to values for average continental crust (Table 7.2). The only two significant regional differences were observed for barium and chromium in West Harrison Bay. Sediment barium concentrations were 200 μg/g higher in West Harrison Bay than in the other Study Area regions (Figure 7.2), and chromium values were about 30 μg/g higher than the averages for the other

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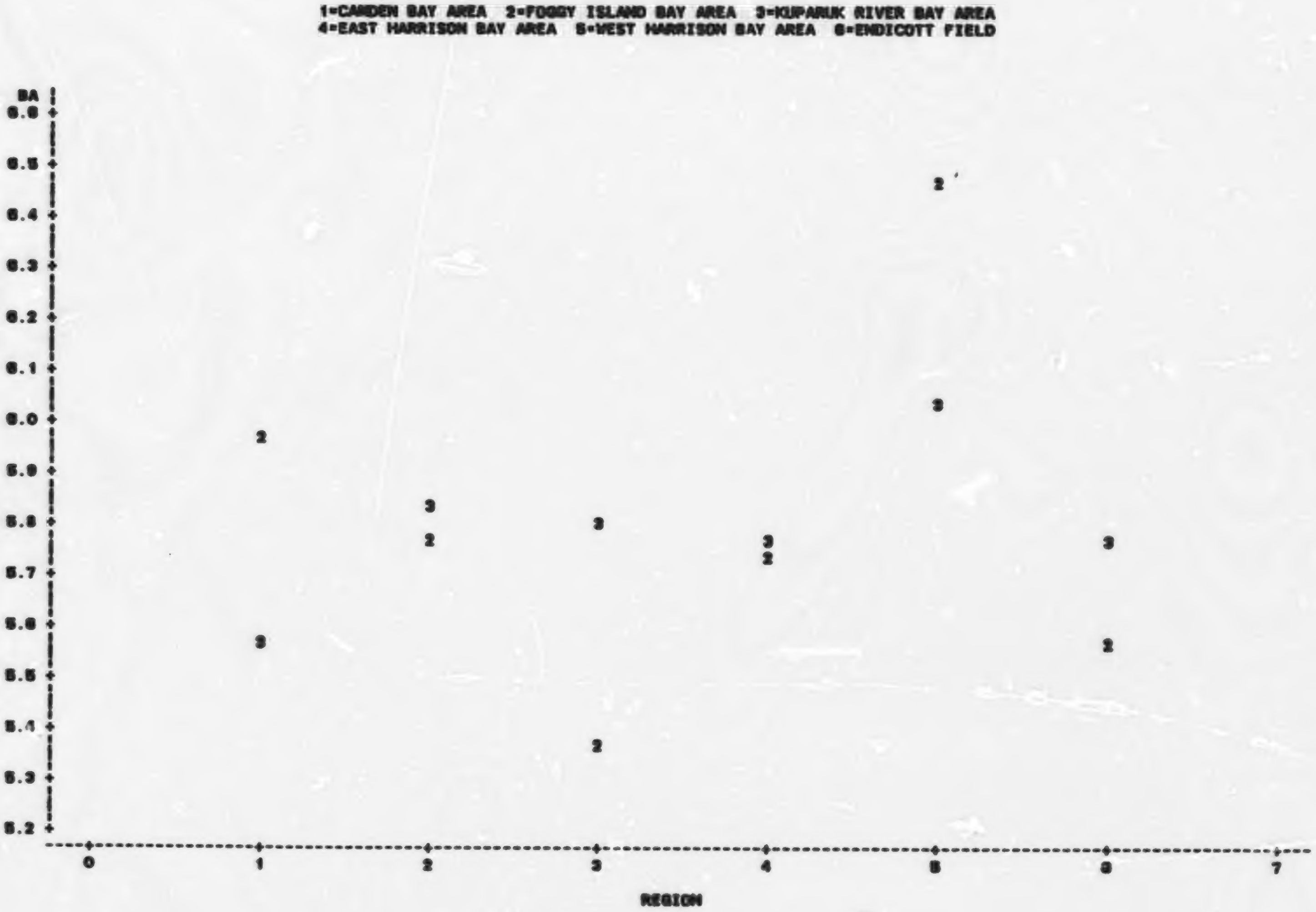

FIGURE 7.1 MEAN LOG BARIUM CONCENTRATIONS IN FINE SEDIMENTS FOR YEAR-2 AND YEAR-3.

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TABLE 7.2 REGIONAL SUMMARY OF TRACE METALS, TOTAL ORGANIC CARBON, AND PERCENT MUD IN THE MUD FRACTION OF STUDY AREA REGIONAL SEDIMENTS[a]

Metals[b] (µg/g)	Camden Bay Area	Foggy Island Bay Area	Endicott Field	Kuparuk River Bay Area	East Harrison Bay Area	West Harrison Bay Area	Average Continental Crust[c]
Ba	318	330	290	268	315	514	500
Cd	0.16	0.19	0.23	0.19	0.16	0.13	0.11
Cr	81	75	68	76	90	112	100
Cu	24.6	20.8	18.1	20.3	24.9	21.3	50
Pb	15.5	11.2	9.8	10.1	13.1	11.8	14
V	114	113	97	112	130	116	160
Zn	92	92	78	90	100	94	75
TOC (mg/g)	6.6	6.3	5.3	9.5	9.0	10.7	-
Mud (%)	27	21	12	35	43	37	-

[a] Year-2 and Year-3 geometric means

[b] Dry weight

[c] Bowen, 1979

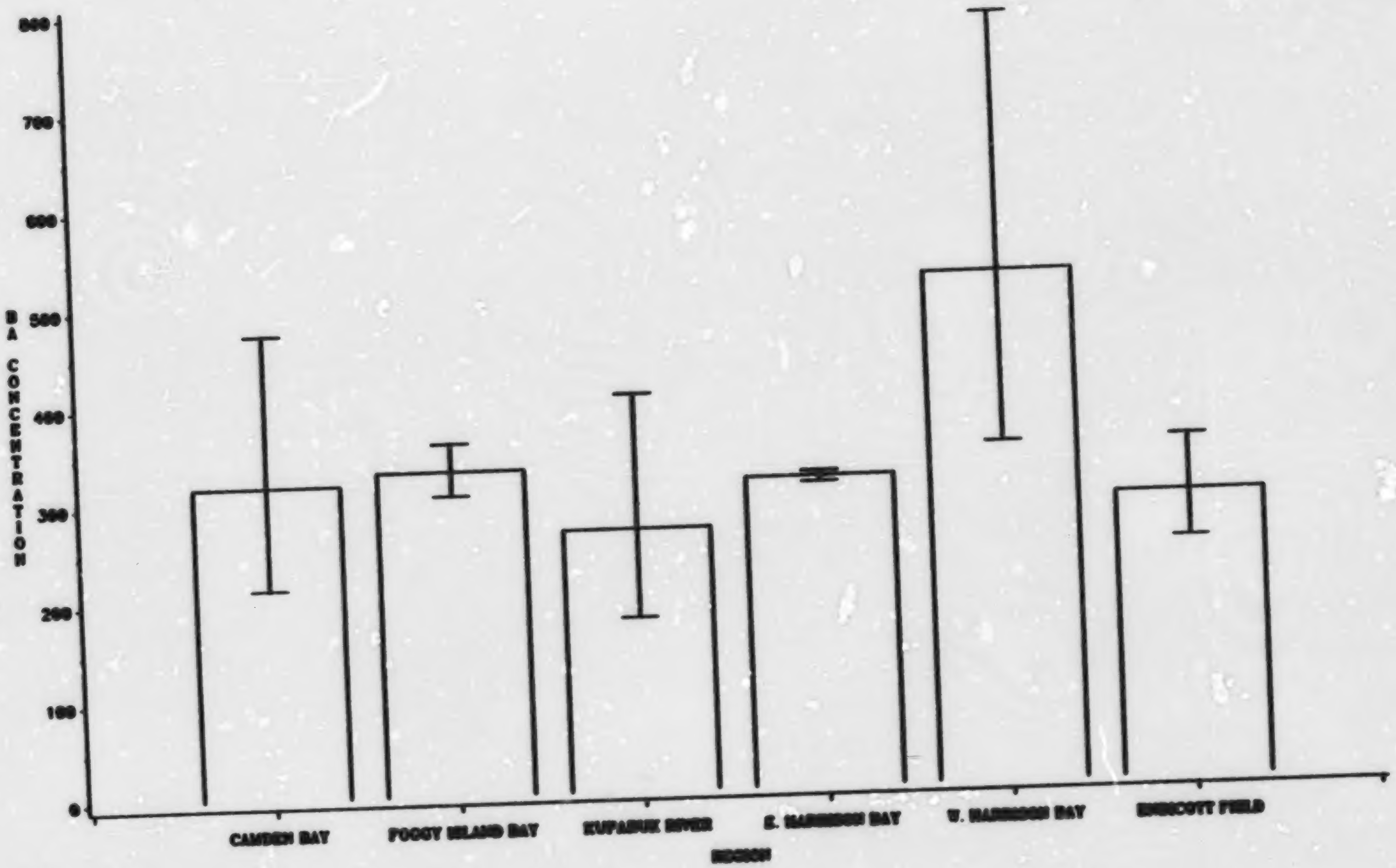

FIGURE 7.2 TWO-YEAR GEOMETRIC MEAN FOR TOTAL BARIUM CONCENTRATIONS IN FINE-GRAINED SEDIMENTS (MUD) FROM SIX REGIONS OF THE STUDY AREA. BRACKETS INDICATE 95 PERCENT CONFIDENCE LIMITS.

regions (Figure 7.3). The elevated barium and chromium values in Harrison Bay are consistent with the higher observed values for mud from the Colville River, a major source of sediment to the bay. The other five metals did not change significantly between regions as demonstrated by the vanadium data set show in Figure 7.4. This trend is also consistent with data for riverine source muds.

7.2.2.3 Cycling of Metals in Shelf Sediments

The cycling of barium, chromium, vanadium, lead, copper, zinc, and cadmium in shelf sediments has been studied to a limited extent in non-Alaskan marine sediments (Carpenter et al., 1975; Feely et al., 1981; Sholkovitz, 1978; Santschi et al., 1983). The geochemical processes that influence the concentrations of these metals in sediments are not expected to differ greatly in the Beaufort Sea. Barium, chromium, vanadium, and lead, metals primarily associated with crustal minerals, are not readily solubilized or bioaccumulated. The distribution of these crustal elements is controlled by the elemental concentrations in the source materials (e.g., mud, sand) as well as by the degree of physical sorting of grain sizes on the shelf. Biological processes and chemical reactions have a limited effect on the concentrations of these particular elements in sediments.

Copper, zinc, and cadmium are much more soluble in seawater than crustal elements and, therefore, may be more readily released from sediments and made available for bioaccumulation. Most of the biogenic cadmium, for example, is released to the water column before the particles are incorporated into sediments. Copper and zinc, on the other hand, are taken up by suspended particles (e.g., adsorption onto metal oxides or organic matter) or by organisms. As these particles are deposited, only some of the copper and zinc is recycled; the balance is retained in the sediments.

Because much of the particulate cadmium is released to the water column before particles are incorporated into the sediments, the correlations between cadmium and grain size (e.g., $r = 0.3-0.5$), and cadmium and TOC ($r = 0.3$) are weak.

7.2.2.4 Relationships Between Source Materials and Sediment Trace Metal Composition

During the last 20 years, several studies have investigated the sources and movement of sediments in the Beaufort Sea. The major riverine source of sediment is the Colville River, which enters eastern Harrison Bay (Carlson, 1976). According to Naidu et al. (1982), most of the river-borne sediments are eventually deposited in deltas or lagoons. Erosion of shoreline peat, estimated at 1-4 m/yr along some regions of the coast, is

.1150

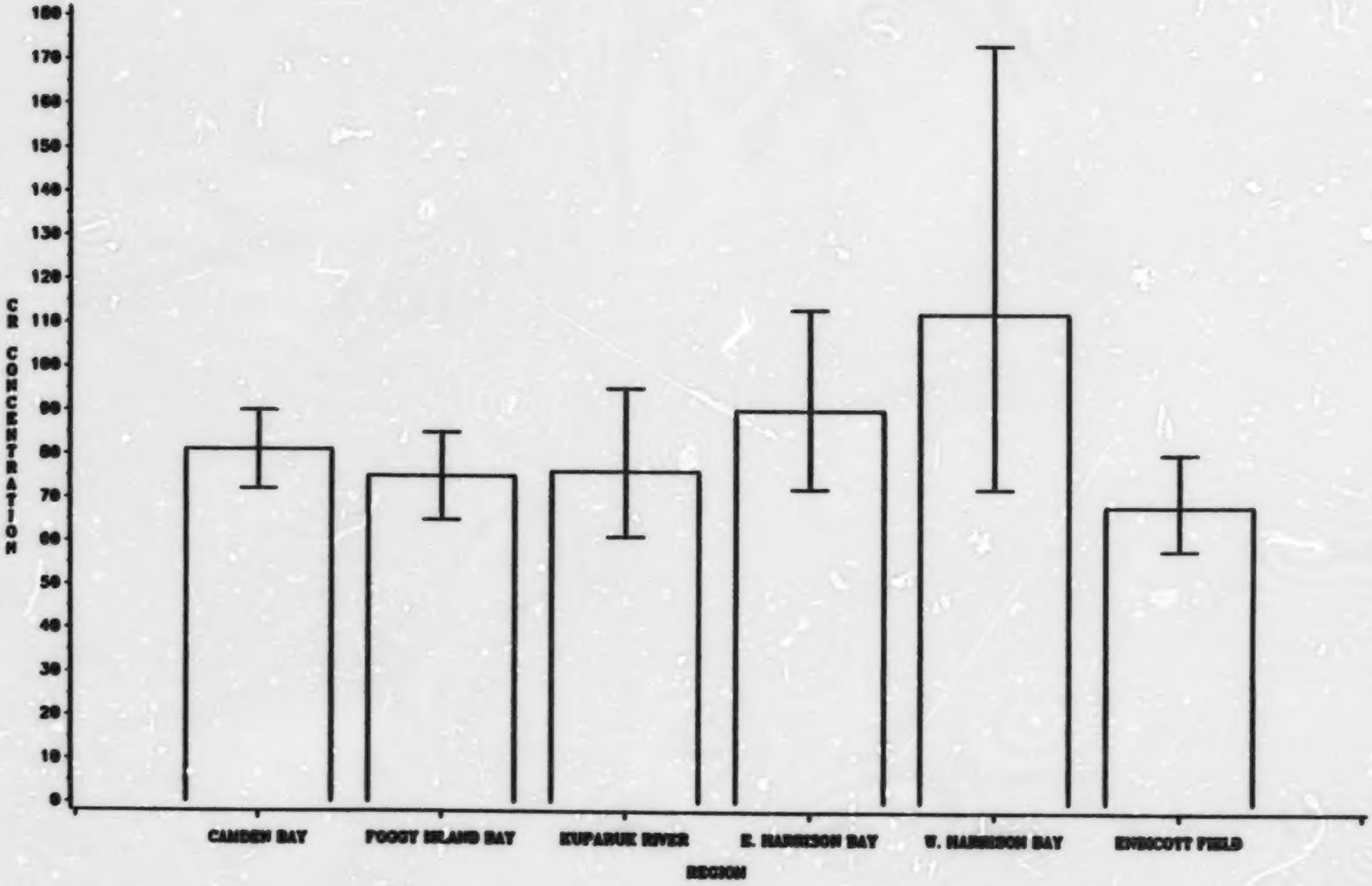

FIGURE 7.3 TWO-YEAR GEOMETRIC MEAN FOR TOTAL CHROMIUM CONCENTRATIONS IN FINE-GRAINED SEDIMENTS (MUD) FROM SIX REGIONS OF THE STUDY AREA. BRACKETS INDICATE 95 PERCENT CONFIDENCE LIMITS.

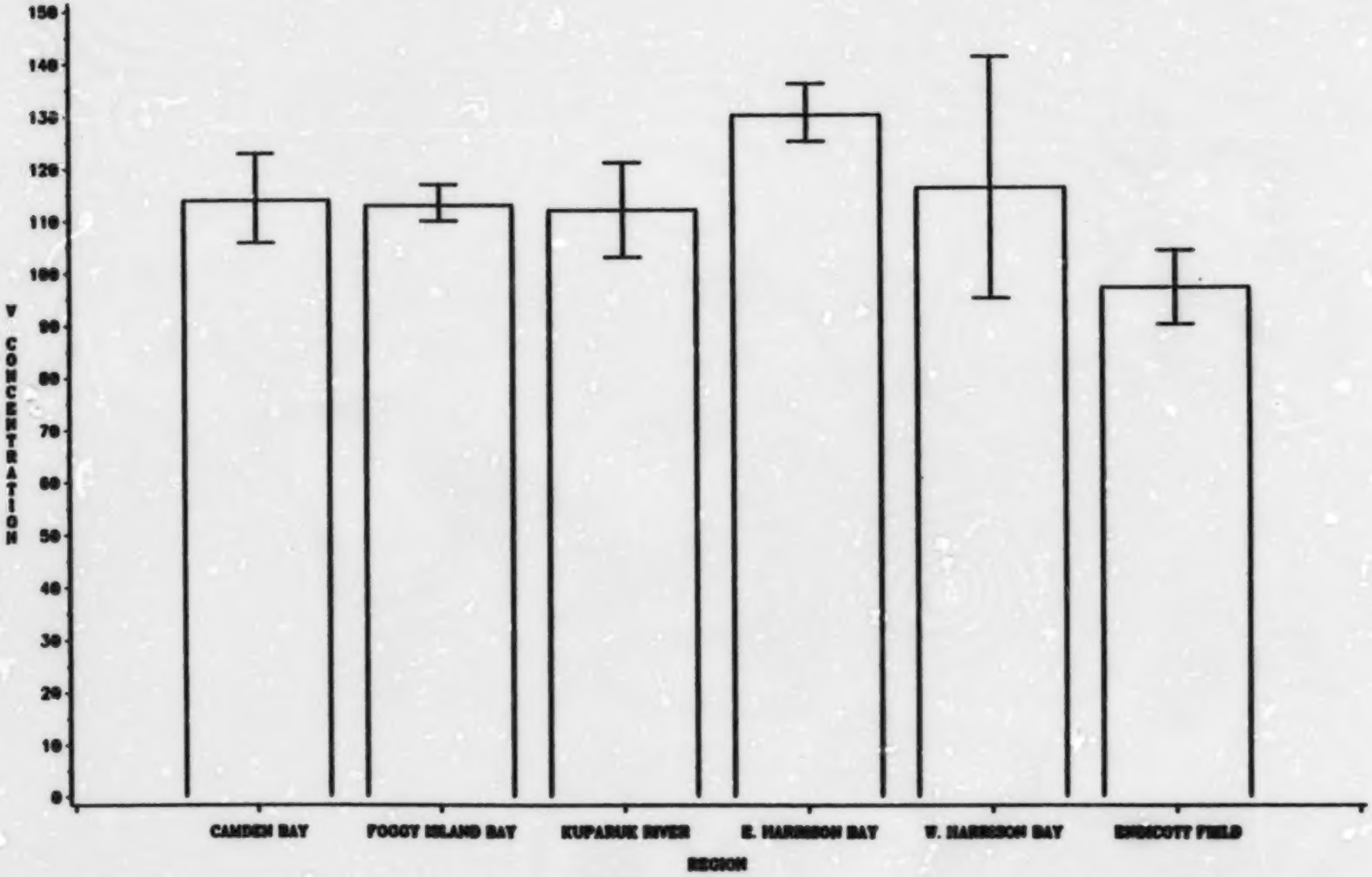

FIGURE 7.4 TWO-YEAR GEOMETRIC MEAN FOR TOTAL VANADIUM CONCENTRATIONS IN FINE-GRAINED SEDIMENTS (MUD) FROM SIX REGIONS OF THE STUDY AREA. BRACKETS INDICATE 95 PERCENT CONFIDENCE LIMITS.

another major source of sediment to the Beaufort Sea (Hume and Schalk, 1967; Short et al., 1974).

The prevailing easterly winds transport both river plumes and resuspended nearshore sediments westward during the open-water season. Westerly storms, which occasionally occur during summer and fall, can be important in the easterly transport of nearshore sediments (Dygas and Burrell, 1976). Ice-scouring and sediment rafting may also be important sediment transport processes.

The broad regional variations in grain size, TOC, and metals of the Beaufort Sea surface sediments have been discussed by Naidu et al. (1982). The general pattern they observed is that percent mud (silt + clay), TOC, and heavy metals in sediment increased with distance offshore. Generally, the middle and outer continental shelf areas are carpeted by poorly sorted sandy muds. The inner shelf and bay sediments are mainly silty sand and sandy silt with minor amounts of clay and gravel. The gravel in the outer shelf sediments may be relict deposits, indicating that much of the mud transport on the shelf is apparently bypassing the shelf area and depositing in deeper water. The poorly sorted sediments on the shelf are probably a result of mixing by ice gouging and bioturbation.

The results from Year-1 and Year-2 bulk sediment analyses indicate a good correlation between percent mud in the sediments and trace metal concentrations (Table 7.3). The bulk sediments have high positive correlation coefficients (>0.5) among several metals (Pb, Cr, Cu, Zn, and V) and TOC, silt, and clay. The other high positive correlations are among copper, chromium, lead, vanadium, and zinc. Cadmium and barium are weakly correlated (0.2-0.5) with TOC, silt, and clay. There are no strong negative correlations. These correlations support previous studies in which grain size and TOC are reported to control the distribution of these seven metals in the Beaufort Sea sediments.

Data for the mud fraction of Year-2 and Year-3 sediments were also analyzed for metals in an attempt to normalize for differences due to grain size and TOC. Correlation coefficients for these data are shown in Table 7.4. Generally, the results were as expected because the TOC data used for the correlations were for bulk sediments, rather than the mud fraction. The lack of strong correspondence between percent mud and metal content in the bulk fraction indicates that the concentrations of metals do not directly relate to the percent mud in the sediment. In the mud fraction analyzed, the only strong correlations (>0.7) were between lead and copper, lead and vanadium, copper and zinc, copper and vanadium, and zinc and vanadium. These interactions are most likely due to change in grain size or TOC concentrations within the mud fraction of these sediments.

TABLE 7.3 INTERNAL CORRELATIONS AMONG ALL CHEMICAL VARIABLES FOR YEAR-1 AND YEAR-2 BULK SEDIMENTS.

PEARSON CORRELATION COEFFICIENTS / PROB > |R| UNDER HO:RHO=0 / NUMBER OF OBSERVATIONS

	BA	CD	CR	CU	PB	V	ZN	TOC	MUD
BA	1.00000 0.0000 239	-0.08420 0.3230 239	0.58167 0.0001 239	0.36786 0.0001 239	0.50883 0.0001 239	0.58740 0.0001 239	0.42296 0.0001 239	0.47594 0.0001 239	0.44802 0.0001 239
CD	-0.08420 0.3230 239	1.00000 0.0000 239	0.37133 0.0001 239	0.58188 0.0001 239	0.30280 0.0001 239	0.41801 0.0001 239	0.47512 0.0001 239	0.41840 0.0001 239	0.50878 0.0001 239
CR	0.58167 0.0001 239	0.37133 0.0001 239	1.00000 0.0000 239	0.81677 0.0001 239	0.74288 0.0001 239	0.94875 0.0001 239	0.82882 0.0001 239	0.63302 0.0001 239	0.81857 0.0001 239
CU	0.36786 0.0001 239	0.58188 0.0001 239	0.81677 0.0001 239	1.00000 0.0000 239	0.53882 0.0001 239	0.84039 0.0001 239	0.69827 0.0001 239	0.52357 0.0001 239	0.75007 0.0001 239
PB	0.50883 0.0001 239	0.30280 0.0001 239	0.74288 0.0001 239	0.53882 0.0001 239	1.00000 0.0000 239	0.78870 0.0001 239	0.79584 0.0001 239	0.59598 0.0001 239	0.57554 0.0001 239
V	0.58740 0.0001 239	0.41801 0.0001 239	0.94875 0.0001 239	0.84039 0.0001 239	0.78870 0.0001 239	1.00000 0.0000 239	0.86880 0.0001 239	0.68125 0.0001 239	0.82331 0.0001 239
ZN	0.42296 0.0001 239	0.47512 0.0001 239	0.82882 0.0001 239	0.69827 0.0001 239	0.79584 0.0001 239	0.86880 0.0001 239	1.00000 0.0000 239	0.64133 0.0001 239	0.71283 0.0001 239
TOC	0.47594 0.0001 239	0.41840 0.0001 239	0.63302 0.0001 239	0.52357 0.0001 239	0.59598 0.0001 239	0.68125 0.0001 239	0.64133 0.0001 239	1.00000 0.0000 278	0.69947 0.0001 278
MUD	0.44802 0.0001 239	0.50878 0.0001 239	0.81857 0.0001 239	0.75007 0.0001 239	0.57554 0.0001 239	0.82331 0.0001 239	0.71283 0.0001 239	0.69947 0.0001 278	1.00000 0.0000 281

TABLE 7.4 INTERNAL CORRELATIONS AMONG ALL CHEMICAL VARIABLES FOR YEAR-2 AND YEAR-3 FINE SEDIMENTS.

PEARSON CORRELATION COEFFICIENTS / PROB > |R| UNDER HO:RHO=0 / NUMBER OF OBSERVATIONS

	BA	CD	CR	CU	PB	V	ZN	TOC	MUD
BA	1.00000 0.0000 232	-0.10572 0.1062 232	0.25489 0.0001 232	0.28049 0.0001 232	0.33368 0.0001 232	0.22420 0.0006 232	0.11578 0.0784 232	0.21889 0.0008 231	0.20372 0.0018 232
CD	-0.10572 0.1062 232	1.00000 0.0000 232	-0.41855 0.0001 232	0.01058 0.8727 232	-0.06679 0.3111 232	-0.16350 0.0126 232	-0.05898 0.3711 232	0.04275 0.5179 231	-0.11938 0.0695 232
CR	0.25489 0.0001 232	-0.41855 0.0001 232	1.00000 0.0000 232	0.25488 0.0001 232	0.01757 0.7900 232	0.41559 0.0001 232	0.33622 0.0001 232	0.06255 0.3439 231	0.20810 0.0014 232
CU	0.28049 0.0001 232	0.01058 0.8727 232	0.25488 0.0001 232	1.00000 0.0000 232	0.66386 0.0001 232	0.80668 0.0001 232	0.59742 0.0001 232	0.32185 0.0001 231	0.30723 0.0001 232
PB	0.33368 0.0001 232	-0.06679 0.3111 232	0.01757 0.7900 232	0.66386 0.0001 232	1.00000 0.0000 232	0.50321 0.0001 232	0.31888 0.0001 232	0.28281 0.0001 231	0.21571 0.0009 232
V	0.22420 0.0006 232	-0.16350 0.0126 232	0.41559 0.0001 232	0.80668 0.0001 232	0.50321 0.0001 232	1.00000 0.0000 232	0.63325 0.0001 232	0.29252 0.0001 231	0.33043 0.0001 232
ZN	0.11578 0.0784 232	-0.05898 0.3711 232	0.33622 0.0001 232	0.59742 0.0001 232	0.31888 0.0001 232	0.63325 0.0001 232	1.00000 0.0000 232	0.29434 0.0001 231	0.33424 0.0001 232
TOC	0.21889 0.0008 231	0.04275 0.5179 231	0.06255 0.3439 231	0.32185 0.0001 231	0.28281 0.0001 231	0.29252 0.0001 231	0.29434 0.0001 231	1.00000 0.0000 232	0.65793 0.0001 232
MUD	0.20372 0.0018 232	-0.11938 0.0695 232	0.20810 0.0014 232	0.30723 0.0001 232	0.21571 0.0009 232	0.33043 0.0001 232	0.33424 0.0001 232	0.65793 0.0001 232	1.00000 0.0000 234

Shoreline peat samples were analyzed for metals in both the bulk and mud fractions. The results are presented in Table 7.5 for mean concentrations in two regions of the Beaufort Sea. These results indicate that peat was not significantly different from the offshore sediments in trace metal content. Also, there was very little difference between the concentration of metals in the bulk or mud fraction of peat. The TOC content of peat was approximately 10 times higher than that in shelf sediments. If the peat samples collected and analyzed are representative of the Beaufort Sea coastal peat, peat cannot have a major influence on the concentration of metals in sediments, assuming that the TOC concentration of sediment is derived from peat. Because the sediments contain approximately 1 percent TOC, the sediment should contain less than 10 percent peat.

River sediment samples were collected in Year-2 and Year-3 to identify additional potential sources of sediments to the offshore area. The river sediments collected were very different in barium concentration, grain size, and TOC (Tables 7.6 and 7.7). The samples from the Sagavanirktok and Canning Rivers were low in barium. The Colville and Kuparuk River sediments were high in barium, but similar to the Sagavanirktok and Canning Rivers, and shelf sediments for the other six metals. Sediment data from these major rivers suggest that rivers may be a major source of both sediments and trace metals to the Beaufort Sea.

7.2.3 Trace Metal Composition of Tissues

The tissues of amphipods and bivalves were analyzed for metals to determine 1) geographic differences, 2) annual variations in body burdens, 3) relationships between metals in sediment and in tissue of organisms living on or in the sediment, and 4) potential use of sentinel organisms in the BSMP program. Amphipods were collected at nine stations in Year-2. Each sample was analyzed as four replicate composites of whole animals. Bivalves were collected at 10 stations, several were pooled to form 8 samples, and each sample was analyzed as 4 replicate composites of shucked tissue. Only at three stations were bivalves collected for each of the three years.

Geographic trends were examined in Year-2 during which the most extensive tissue sampling occurred. The mean concentrations of metals in amphipod and bivalve tissues are presented in Tables 7.8 and 7.9. The concentration of each metal in the amphipods varied by a factor of approximately three between the lowest and the highest station. There did not appear to be a geographical trend with this limited data set. Although several metals (cadmium, copper, and zinc) appeared to co-vary, there does not appear to be a correlation between mud and the concentrations of metals in tissue from the collection station.

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TABLE 7.5 REGIONAL MEAN CONCENTRATIONS OF METALS IN THE BULK AND MUD FRACTION OF PEAT SAMPLES AND RIVER SEDIMENTS

Metals ($\mu g/g$)[a]	Eastern Study Area (4) Peat Stations "1","2","3"		Western Study Area (4) Peat Stations "5","6","7"		Sagavanirktok River (1)		Colville River (1)	
	Bulk	Mud	Bulk	Mud	Bulk	Mud	Bulk	Mud
Ba	482	485	334	411	102	191	612	953
Cd	0.23	0.23	0.32	0.30	0.29	0.40	0.15	0.27
Cr	51	66	33	65	41	56	46	101
Cu	9.8	11	9.4	9.7	6.3	7.1	8.7	13
V	80	97	55	88	59	84	62	117
Zn	59	68	56	81	62	91	60	106
TOC[b]	13	-	17	-	1.3	-	6.6	-
Mud[b]	66	-	56	-	16	-	69	-

[a] Dry weight

[b] Percent dry weight

Dashes indicate no sample

TABLE 7.6 SUMMARY OF METALS IN MUD FRACTION OF RIVER SEDIMENTS AND REGIONAL MARINE SEDIMENTS[a]

	Canning River	Camden	Sagavanirktok River		Endicott
	(Yr-2)	Bay Area	(Yr-2)	(Yr-3)	Field
Metals, (µg/g)[b]					
Ba	63	318	191	272	290
Cd	0.23	0.16	0.40	0.28	0.23
Cr	81	81	56	81	68
Cu	22	25	19	18	18
Pb	5.8	15	7.1	12	9.8
V	91	114	84	88	97
Zn	92	92	91	87	78

[a] Year-2 and Year-3 geometric mean

[b] Dry weight

TABLE 7.7 SUMMARY OF METALS IN THE MUD FRACTION OF RIVER SEDIMENTS AND REGIONAL MARINE SEDIMENTS

Metals (µg/g)[b]	Kuparuk River (Yr-3)	Kuparuk River Bay Area	Colville River (Yr-2)	Colville River (Yr-3)	East Harrison Bay Area	West Harrison Bay Area
Ba	496	268	953	854	315	514
Cd	0.33	0.19	0.27	0.22	0.16	0.13
Cr	109	76	101	168	90	112
Cu	20.3	20.3	24.0	24.2	24.9	21.3
Pb	8.7	10.1	13.1	9.9	13.1	11.8
V	96	112	117	106	130	116
Zn	102	90	106	97	100	94

[a] Year-2 and Year-3 geometric means

[b] Dry weight

TABLE 7.8 SUMMARY OF METAL CONCENTRATIONS IN TISSUE SAMPLES COLLECTED FROM EASTERN STUDY AREA STATIONS

	1A	1A+1B+1E	1A+1B	2F	3A		4B
Metals (ug/g)[a]	Portlandia	Anonyx	Astarte	Anonyx	Anonyx	Astarte	Anonyx
Ba	98 ± 3	39 ± 3	20 ± 1	36 ± 1	22 ± 1	18 ± 10	22 ± 2
Cr	12 ± 0.6	3.4 ± 0.3	2.5 ± 0.1	2.0 ± 0.3	1.1 ± 0.4	3.0 ± 1.1	0.39 ± 0.08
V	23 ± 0.6	4.2 ± 0.4	2.4 ± 0.2	1.0 ± 0.2	0.6 ± 0.2	5.0 ± 2.0	<D.L.[b]
Pb	5.6 ± 0.7	0.7 ± 0.3	0.3 ± 0.1	<D.L.	<D.L.	0.4 ± 0.3	0.1 ± 0
Cu	35 ± 1	97 ± 4	12 ± 1	77 ± 2	176 ± 8	14 ± 4	131 ± 7
Zn	179 ± 8	134 ± 2	80 ± 5	107 ± 4	124 ± 8	84 ± 17	105 ± 3
Cd	7.6 ± 0.6	1.0 ± 0.5	25 ± 1	0.6 ± 0.1	1.5 ± 0	8.2 ± 1.9	1.0 ± 0.1

[a] Wet Weight

[b] Detection Limit

TABLE 7.9 SUMMARY OF METAL CONCENTRATIONS IN TISSUE SAMPLES COLLECTED FROM WESTERN STUDY AREA STATIONS

	5F	5H		6D		6G		7B + 7C	7E
Metals (µg/g)[a]	Cyrtodaria	Anonyx	Astarte	Macoma	Astarte	Anonyx	Cyrtodaria	Anonyx	Anonyx
Ba	25 ± 5	23 ± 5	17 ± 7	117 ± 16	30 ± 12	60 ± 1	26 ± 3	27 ± 3	55 ± 3
Cr	2.9 ± 0.6	2.0 ± 0.9	1.7 ± 0.4	9.0 ± 1.5	3.1 ± 0.9	1.5 ± 0	2.4 ± 0.7	1.9 ± 0.6	0.7 ± 0.1
V	6.5 ± 1.4	1.6 ±0.6	1.2 ±0.3	21 ± 3	6.8 ± 3.6	0.7 ± 0.2	5.5 ± 0.8	1.6 ± 0.2	0.4 ± 0
Pb	0.5 ± 0.1	<D.L.[b]	0.2 ± 0.1	3.1 ± 0.3	1.0 ± 0.3	0.2 ± 0.1	0.7 ± 0.1	<D.L.	<D.L.
Cu	24 ± 1	129 ± 2	11 ± 2	25 ± 11	23 ± 10	66 ± 2	20 ± 1	154 ± 7	89 ± 7
Zn	75 ± 2	139 ± 8	65 ± 5	168 ± 22	96 ± 16	72 ± 2	66 ± 1	105 ± 6	85 ± 1
Cd	1.5 ± 0.1	1.3 ± 0.4	12 ± 3	4.7 ± 8.7	11 ± 0	0.2 ± 0	1.3 ± 0.1	0.8 ± 0.2	0.4 ± 0.1

[a] Wet weight

[b] Detection Limit

Trace metal data for Alaskan amphipods have been reported in a Nortec (1982) study of the Beaufort Sea Challenge Island drilling fluid disposal site. Table 7.10 compares amphipod tissue trace metal concentrations reported by the Nortec study with the concentrations found in the Year-2 BSMP. With the exception of lead, the mean tissue trace metal concentrations are similar. The mean lead levels reported by Nortec (1982) are two orders of magnitude higher than the values reported in the present study. We do not have an explanation for this apparent disagreement.

The concentrations of metals in bivalves collected at three stations can be compared for three years (Table 7.11). The data from the three years were similar, indicating very little annual variation had occurred for these species at these stations, and indicating that these animals have great potential for use in detecting changes due to anthropogenic inputs.

The bivalve data set was too limited for each species to determine any meaningful geographic trends. The major differences in the bivalve data set appear to be due to differences between species. The concentrations of cadmium in Astarte ranged between 8 and 25 µg/g dry weight. These concentrations are approximately 10 times higher than levels of cadmium found in other bivalve species, including the other filter feeder (Cyrtodaria) collected and the amphipods. This apparent accumulation of cadmium by Astarte, but not by Cyrtodaria, is not clear but may be related to physiological properties of the species. As was noted last year, Cyrtodaria contained lower concentrations of cadmium than other bivalves collected and analyzed. The two additional species of bivalves analyzed in Year-2 (Portlandia and Macoma) contained much higher concentrations of several metals, including barium, chromium, lead, vanadium, and zinc, than did Astarte and Cyrtodaria. Body burdens and sediment trace metal concentrations do not appear to be related. Larger data sets, however, are needed to examine these relationships more completely.

7.3 HYDROCARBON CHEMISTRY

7.3.1. General Framework for Interpretation

The hydrocarbon analyses performed as part of this study generated two types of data. The UV/F data describe gross fluorescence, which is converted to quantitative data based on the arbitrary, but relevant, Prudhoe Bay crude oil standard. The GC-FID and GC/MS data yield the concentrations of individual saturated (normal and isoprenoid alkanes) and aromatic (2- to 5-ring homologous series) hydrocarbons, respectively. The UV/F data may be relatively precise and informative. However, if significant background fluorescence is present in the sample, the UV/F data will be insensitive to subtle compositional

TABLE 7.10 MEAN TRACE METAL CONCENTRATIONS IN ALASKAN AMPHIPOD TISSUES

Metals (ug/g)[a]	Nortec Study (1982)	Year-2 BSMP (1986)
Ba	29 ± 32	36 ± 14
Cr	1.8 ± 0.8	1.6 ± 0.9
Pb	22 ± 2.2	0.19 ± 0.19
Cu	83 ± 26	115 ± 36
Zn	94 ± 20	109 ± 22
Cd	3.8 ± 0.6	0.87 ± 0.41

[a] Wet weight

TABLE 7.11 THREE-YEAR MEAN CONCENTRATIONS OF TRACE METALS IN BIVALVE TISSUES AT THREE STUDY AREA STATIONS

	3A Astarte			5F Cyrtodaria			6D Astarte		
Metals (µg/g)[a]	Yr-1	Yr-2	Yr-3	Yr-1	Yr-2	Yr-3	Yr-1	Yr-2	Yr-3
Ba	8	19	12	17	26	19	30	30	33
Cd	9.3	8.2	9.2	1.4	1.5	1.5	11	11	13
Cr	2.4	3.0	2.3	3.2	2.9	2.7	4.5	3.1	3.8
Cu	12	15	11	16	24	14	28	23	26
Pb	0.6	0.5	0.5	0.5	0.5	0.7	0.8	1.0	0.9
V	1.9	5.0	2.1	3.3	6.5	4.8	5.3	6.8	7.0
Zn	73	84	66	68	75	60	96	97	94

[a] Wet weight

changes and increments of sub-ppm inputs of "new" material (i.e., pollutants). GC-FID and GC/MS, on the other hand, yield accurate and precise data at lower quantitative levels. In addition, key source-diagnostic ratios (Tables 7.12 and 7.13) can be calculated and also used, along with quantitative data (Tables 7.14 and 7.15), to address changes in the composition of ambient hydrocarbon concentrations over time. UV/F data were generated only for sediment samples from Year-1 and for animal tissues in all years. It was determined in Year-1 that a large background UV/F signal existed in the sediment and that continued use of UV/F as a sediment hydrocarbon monitoring technique would not be useful in this program. GC-FID and GC/MS data were generated for all samples.

7.3.2 Review of Historic Data

The distribution of hydrocarbons (Kaplan and Venkatesan, 1981; Shaw et al., 1979; Shaw, 1981; Venkatesan and Kaplan, 1982) in Beaufort Sea sediments has been documented. Shaw et al. (1979) examined the hydrocarbon geochemistry of nearshore sediments at 20 stations between Point Barrow and Barter Island. Total hydrocarbon concentrations in the nearshore sediments ranged between 0.3 and 20 µg/g dry sediment. Lowest concentrations were found in sediments from the Canning River delta; highest concentrations were found in sediments from the Colville River delta.

The saturated hydrocarbons were dominated by n-alkanes, ranging in chain length from 23 to 31 carbon atoms, with a strong odd-even preference and no unresolved complex mixture (UCM) evident. This distribution is consistent with a prevalent biogenic input of terrigenous plant material, most likely resulting from transport of riverine suspended particulate matter during the spring runoff.

Shaw et al. (1979) also examined sources of aromatic hydrocarbons in nearshore sediments by using the alkyl homologue distributions of selected aromatic hydrocarbon series analyzed by gas chromatography/mass spectrometry (GC/MS). Distributions characteristic of both pyrogenic and petrogenic origins were observed, with the geographic distribution of pyrogenic aromatic compounds indicative of a long-range transport source of anthropogenic combustion products rather than localized inputs. The analysis of alkyl homologue distributions also indicated that seep oil from the Cape Simpson area, Mead River coal, and Prudhoe Bay crude oil were not the sources of aromatic hydrocarbons in the region. The presence of cadalene, retene, and simonellite in many sediment samples indicated that early diagenesis of plant material (possibly including peat) contributed to the polycyclic aromatic hydrocarbon (PAH) assemblages in the sediments. PAHs of pyrolytic origin were most abundant in sediments from the Hulahula River delta; fossil

TABLE 7.12 SATURATED HYDROCARBON PARAMETER SOURCE RATIOS DETERMINED BY HIGH RESOLUTION FLAME IONIZATION DETECTION GAS CHROMATOGRAPHY (GC-FID) AND USED TO TEST NULL HYPOTHESES Ho2 (SEDIMENT HYDROCARBON SOURCES) AND Ho4 (BIVALVE HYDROCARBON SOURCES)

Parameter	Relevance
ISO/ALK	Measures the relative abundance of branched isoprenoid alkanes to straight chain alkanes in the same boiling range; Useful indicators of biodegradation.
LALK/TALK	Diagnostic alkane compositional ratio used to determine the relative abundance of n-C10 to n-C20 alkanes (characteristic of light crude and refined oils) to total alkanes which includes those of biogenic (background) origin.
PRIS/PHY	Source of phytane is mainly petroleum while pristane is derived from both biological matter and oil. In "clean" samples, this ratio is very high and decreases and oil is added.
TOT/TOC or n-alkanes/TOC	The ratio of total saturated hydrocarbons (TOT) or n-alkanes (subset of TOT) to total organic carbon (TOC) is used to monitor oil inputs. In sediments receiving "normal" pollutant inputs within a given region, a specific TOT/TOC ratio is characteristic of the "geochemical provence". Small (tens of ppm) additions of petroleum to sediment cause the ratio to increase dramatically because n-alkanes increase but TOC does not.
OEPI	Odd-even carbon preference index; Describes the relative amounts of odd and even chain alkanes within a specific boiling range; As oil additions increase, the OEPI is lowered.

TABLE 7.13 PAH DIAGNOSTIC SOURCE PARAMETERS AND RATIOS DETERMINED BY HIGH RESOLUTION GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS) AND USED TO TEST NULL HYPOTHESES Ho2 (SEDIMENT HYDROCARBON SOURCES) AND Ho4 (BIVALVE HYDROCARBON SOURCES)

Parameters	Relevance
Alkyl Homologue Distribution (AHD)	Used to assess the relative importance of fossil fuel and combustion PAH sources. The abundance of alkyl-substituted PAHs within a given aromatic series, relative to the parent compound, can be a sensitive indicator of hydrocarbons. Combustion sources are generally characterized by a greater relative abundance of parent compounds while petroleum contains greater relative quantities of the alkyl homologues.
FFPI	Fossil Fuel Pollution Index[a]; Ratio of fossil fuel-derived PAH to total (fossil + pyrogenic + diagenic) PAH. FFPI for fossil PAH = 100; FFPI for combustion PAH = 0.
Specific PAH ratios	For example, P/D is an excellent indicator of petrogenic input.
PAH/TOC	Analogous to TOT/TOC ratio.

[a] $\mathrm{FFPI} = (\mathrm{N} + \mathrm{F} = \mathrm{P} + \mathrm{D})/\Sigma\ \mathrm{PAH}$

$$\Sigma\ \mathrm{PAH} = \mathrm{N} + \mathrm{F} + \mathrm{P} + \mathrm{D} + \mathrm{FLAN} + \mathrm{PYRN} + \mathrm{BAA} + \mathrm{CHRY} + \mathrm{BAP} + \mathrm{BEP} + \mathrm{BFA} + \mathrm{PERY}$$

TABLE 7.14 SATURATED HYDROCARBON QUANTITATIVE PARAMETERS DETERMINED BY HIGH RESOLUTION FLAME IONIZATION DETECTION GAS CHROMATOGRAPHY (GC-FID) AND USED TO TEST NULL HYPOTHESES Ho1 (SEDIMENT CONCENTRATIONS) AND Ho3 (BIVALVE CONCENTRATIONS)

Parameter	Relevance
TALK	Quantifies the total n-alkanes (n-C10 to n-C34).
LALK	Sum of low molecular weight n-alkanes (n-C10 to n-C20); Crude petroleum is high in these alkanes. Unpolluted samples are low in many LALKs.
PRIS	Isoprenoid 1708 (Pristane); An abundance of pristane in sediments is indicative of recent biogenic inputs.
PHY	Isoprenoid 1810 (Phytane); Uncontaminated sediments are low in phytane but crude oil has significant amounts of this isoprenoid.
TOT	Total saturated hydrocarbons (resolved plus unresolved).
UCM	Unresolved Complex Mixture; Generally a feature of weathered petroleum; Microbial activity can also result in formation of UCM.
Resolved Hydrocarbons	Can be characteristic of both biogenic and petrogenic sources; However, the ratio of unresolved to resolved can be used to distinguish between hydrocarbon sources.

TABLE 7.15 PAH QUANTITATIVE PARAMETERS DETERMINED BY HIGH RESOLUTION GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS) AND USED TO TEST NULL HYPOTHESES Ho1 (SEDIMENT CONCENTRATIONS) AND Ho3 (BIVALVE CONCENTRATIONS)

Parameter	Relevance
N	Naphthalene Series (C0N + C1N + C2N + C3N + C4N).
F	Fluorene Series (C0F + C1F + C2F + C3F).
P	Phenanthrene Series (C0P + C1P + C2P + C3P + C4P).
D	Dibenzothiophene Series (C0D + C1D + C2D + C3D).
PAH	4- and 5-ring polynuclear aromatic hydrocarbons (FLAN + PYEN + BAA + CHRY + BFA + BAP + BEP + PERY); Origin is pyrogenic (combustion of fossil and wood fuels).
Σ PAH	The sum of 2- to 5-ring polynuclear aromatic hydrocarbons (N + F + P + D + PAH); In conjunction with the PAH parameter, can be used to determine relative contributions of pyrogenic and petrogenic sources.

PAHs were most abundant in sediments from Smith Bay, Cape Halkett, Egg Island, and Stockton Island.

The hydrocarbon geochemistry of the Beaufort Sea outer continent shelf has been studied by Kaplan and Venkatesan (1981) and Venkatesan and Kaplan (1982). The range of total hydrocarbon concentrations reported was 20-50 μg/g dry sediment, which is slightly greater than that found in the nearshore sediments. Whether these differences are due to differences in the analytical methods employed or to a greater abundance of fine-grained, organic-rich sediments in the OCS region was not investigated. As with the nearshore sediments, the major source of saturated hydrocarbons in offshore sediments was found to be debris from higher plants, with no evidence of a UCM indicative of petroleum inputs.

A marine biogenic origin for some of the organic matter was also indicated by the occurrence of the hydrocarbons pristane and n-heptadecane. The occurrence of several alkanes, together with steranes, diterpanes, and triterpanes also attested to the biogenic origin of the organic matter. Measurable concentrations of aromatic hydrocarbons were found in almost all the Beaufort Sea OCS sediments examined. The distribution of alkyl homologues determined by GC/MS was found to be characteristic of a pyrogenic origin. Thus, the available organic geochemical data for the region indicate that hydrocarbons found in nearshore and offshore sediments originate primarily through natural processes, with little evidence of anthropogenic petroleum inputs.

In general, the hydrocarbon concentrations in Beaufort Sea sediments are somewhat elevated in comparison to other OCS sediments. Of more significance, however, is the composition of the hydrocarbons which, because they are largely fossil-derived, differs from most other shelf sediments.

Data on the concentrations of hydrocarbons in bivalves from the region are sparse. Shaw (1981) reported that low levels of hydrocarbons occur in bivalves from the area. Isopods (Saduria entomon) collected off the Sag River delta contained only traces of hydrocarbons and no resolved aromatics. However, tissues of isopods collected from the vicinity of Challenge Island contained a mean of 1.17 ppm resolved light aromatics (benzene through trimethylnaphthalene).

7.3.3 Offshore Sediments

7.3.3.1 Overview of Hydrocarbon Data

The analytical results have been summarized in Section 6 of this report and are presented in detail in Appendix C. The three-year geometric means of total saturated hydrocarbon concentrations in the offshore surface sediments ranged from

2.0 (0.8, 5.6) µg/g at Station 5(1) in the Prudhoe Bay area to 52 (33,81) µg/g at Station 6B in the East Harrison Bay area (note that numbers in parentheses represent the lower and upper 95 percent confidence limits). Figure 7.5 presents the summary of the saturated and the total two- to five-ring PAH data for the Study Area. Although a significant degree of within-station variability was observed at several stations over the course of the three-year study (Figure 7.6), the trends depicted in Figure 7.5 generally held for the entire program. To reinforce the overall trend in hydrocarbon concentrations on a regional basis, consider Figures 7.7 through 7.10 in which the three-year geometric means with error bars are depicted for total saturated hydrocarbon parameters. Stations in the Harrison Bay region contained the greatest concentrations of hydrocarbon compounds, with those stations in the East Harrison Bay area, nearest the Colville River, generally having the highest values. A clear gradient of hydrocarbon concentrations was observed in the Station 6B, 6C and 6D transect offshore. The concentration gradient is discussed more fully in Section 8.

Total PAH concentrations also followed the general overall station pattern, with concentrations ranging from approximately 0.11 µg/g at Station 5(1) to 4.2 µg/g at Station 6B.

Determination of concentrations of hydrocarbons as "equivalents" of Prudhoe Bay crude oil was made in the Year-1 study. Total hydrocarbons, as determined from UV/F data, ranged from 7.5 to 310 µg/g in Year-1. Note that the two sets of values (i.e., those determined from GC-FID and those from UV/F) are not directly comparable because GC-FID measurements were designed to measure saturated hydrocarbons, but UV/F data reflect a total (saturate plus aromatics) hydrocarbon value in "Prudhoe Bay crude oil equivalents." Nevertheless, the GC-FID and UV/F data were highly correlated ($r = 0.88$). Taking mean data from each Year-3 station, the area-wide ratio of saturates (GC-FID) to total (UV/F) is 0.34 ± 0.11.

7.3.3.2 UV/Fluorescence

The UV/F spectral characteristics of the sediment extract were quite uniform throughout the Study Area. As illustrated in Figure 7.11, which depicts representative spectra of sediment UV/F and PBC, the major spectral bands of Study Area sediments are at 355 nm, corresponding to the 3-ringed aromatics; 312 nm, corresponding to the 2-ringed aromatics; and the spectral doublet corresponding to the compound perylene of diagenetic origin. Spectral characteristics of PBC are similar, with maxima at 312 and 355 nm, although the 312 nm peak shows greater abundance than the 355 nm peak. No perylene doublet is observed in the oil. Due to the large background fluorescence in the area's sediments, it is highly doubtful whether UV/F results will be effective in detecting small incremental additions of petroleum hydrocarbons to the sediment.

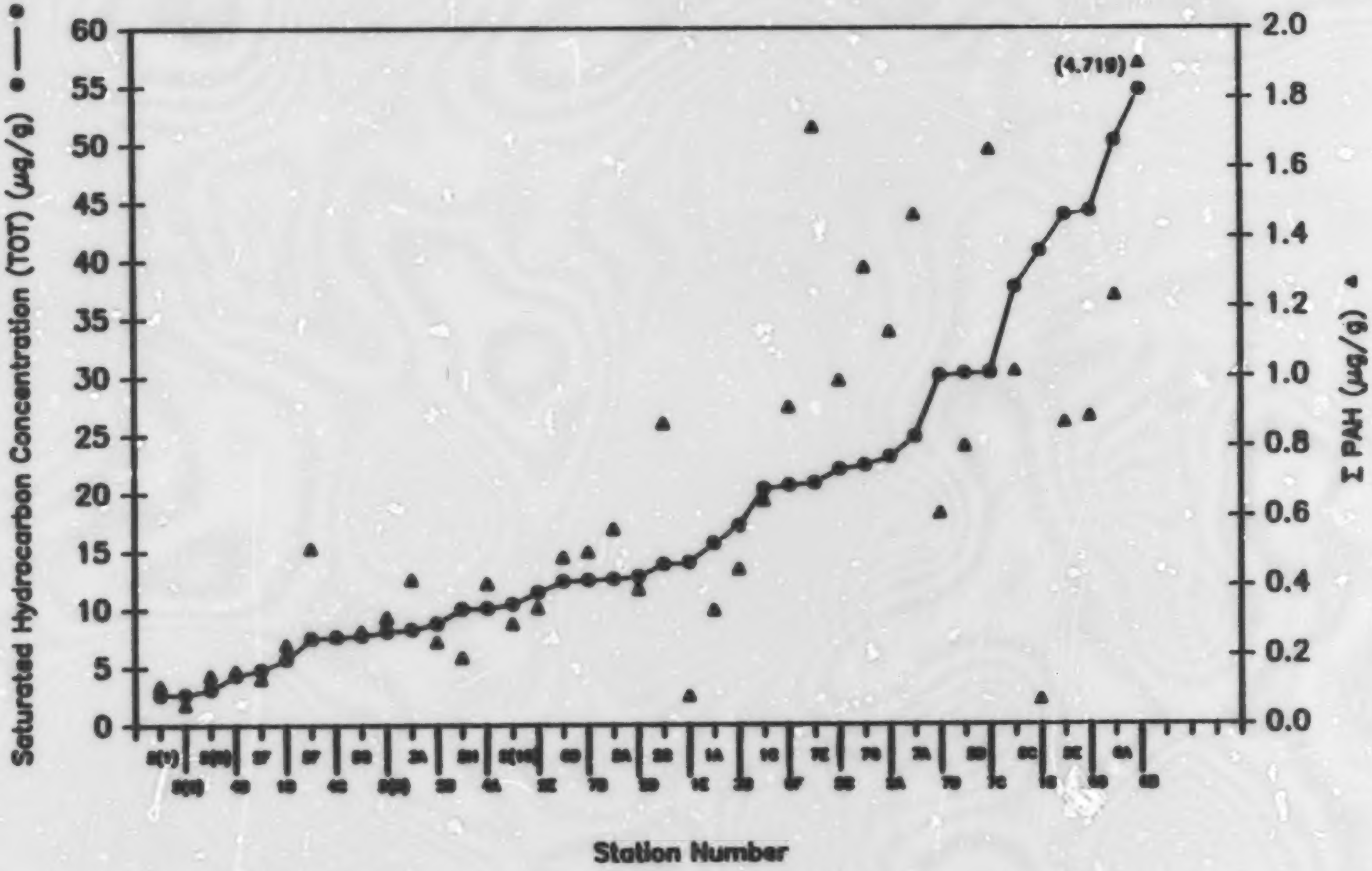

FIGURE 7.5 THREE-YEAR MEAN CONCENTRATIONS OF TOTAL SATURATED HYDROCARBONS (TOT) AND TOTAL PAH.

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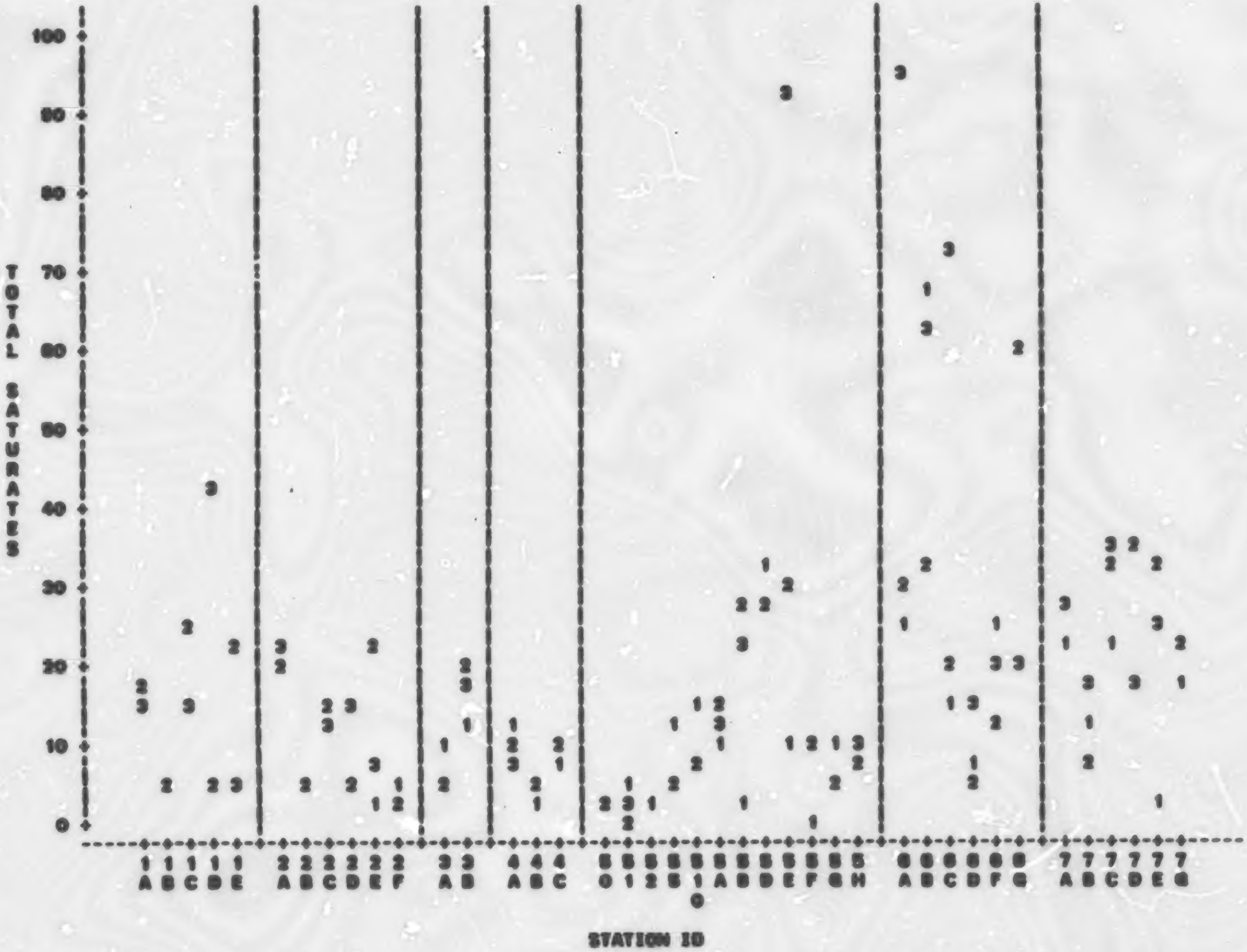

FIGURE 7.6 GEOMETRIC MEAN TOTAL SATURATED HYDROCARBON CONCENTRATIONS (μg/g) FOR YEAR-1, YEAR-2, AND YEAR-3 BULK SEDIMENTS (PLOT SYMBOLS REPRESENT YEAR).

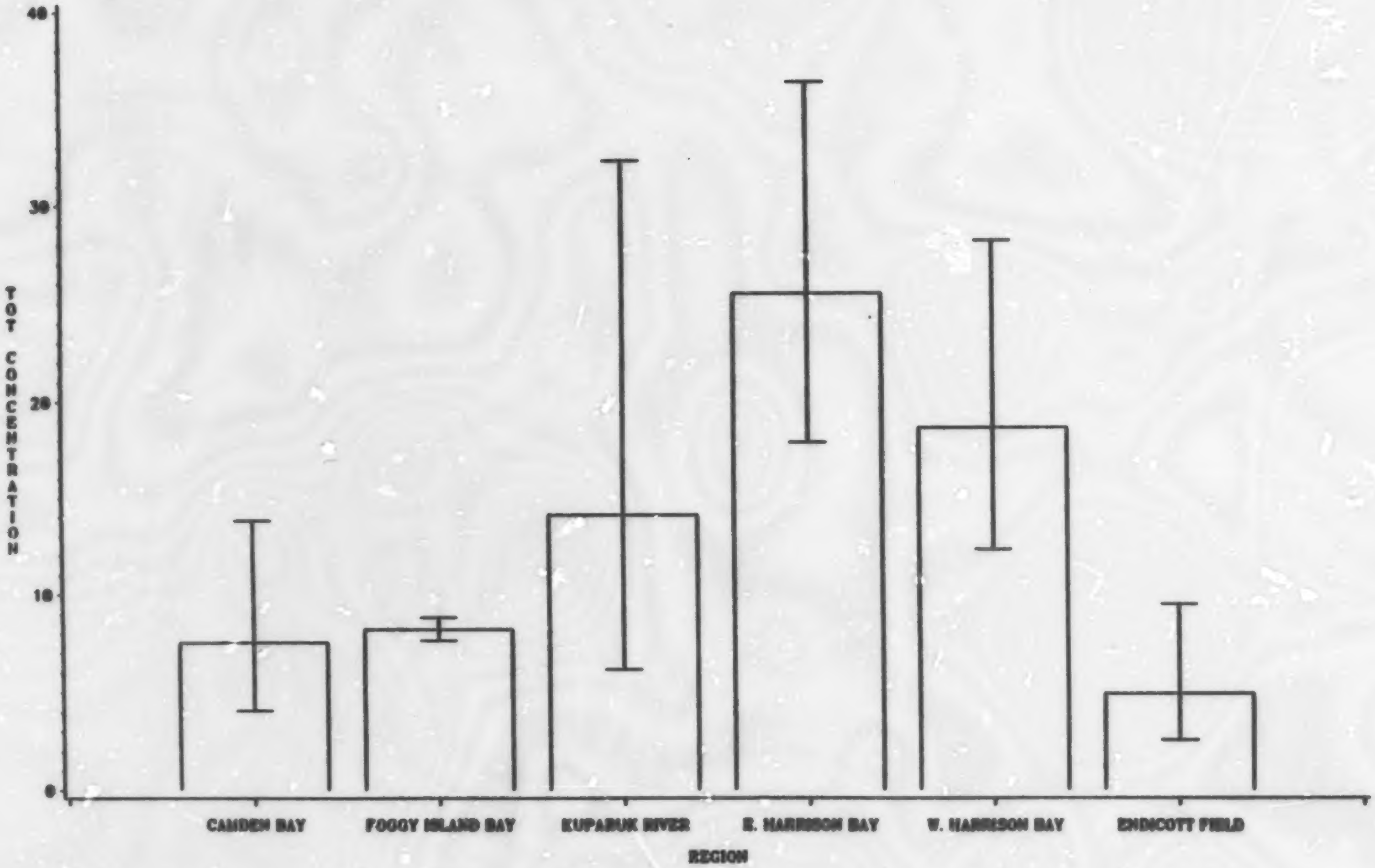

FIGURE 7.7 THREE-YEAR GEOMETRIC MEAN TOTAL SATURATED HYDROCARBON (TOT) CONCENTRATIONS (BRACKETS INDICATE 95 PERCENT CONFIDENCE LIMITS)

TABLE 7.17 SUMMARY OF SEVERAL KEY SATURATED HYDROCARBON PARAMETERS AND DIAGNOSTIC RATIOS[a]

Station	LALK/TALK			PRIS/PHY			ISO/ALK		
	Yr-1	Yr-2	Yr-3	Yr-1	Yr-2	Yr-3	Yr-1	Yr-2	Yr-3
1A	-	0.08	0.08	-	1.8	2.1	-	0.38	0.42
1B	-	0.15	0.15	-	1.8	2.1	-	0.46	0.48
1C	-	0.19	0.17	-	1.5	1.7	-	0.55	0.62
1D	-	0.07	0.09	-	2.3	2.2	-	0.29	0.20
1E	-	0.09	0.09	-	1.8	2.2	-	0.13	0.19
2A	-	0.17	0.16	-	1.5	1.9	-	0.43	0.45
2B	-	0.15	0.20	-	1.8	3.0	-	0.44	0.71
2C	-	0.20	0.16	-	1.5	1.6	-	0.55	0.56
2D	-	0.11	0.15	-	1.7	2.0	-	0.38	3.37
2E	0.32	0.17	0.16	2.5	1.6	2.2	0.44	0.41	0.49
2F	0.27	0.20	0.34	2.6	1.9	2.0	0.48	0.44	0.41
3A	0.18	0.12	0.13	2.1	1.9	2.2	0.45	0.45	0.45
3F	0.18	0.14	0.12	2.0	1.7	2.3	0.44	0.42	0.44
4A	0.18	0.15	0.19	2.4	1.6	2.5	0.43	0.39	0.43
4B	0.27	0.16	0.17	2.3	1.9	2.2	0.44	0.42	0.44
4C	0.27	0.14	0.16	2.3	1.7	2.3	0.43	0.42	0.41
5(0)	-	0.21	0.19	-	2.0	2.3	-	0.41	0.39
5(1)	0.24	0.20	0.31	2.3	2.0	2.1	0.46	0.35	0.25
5(5)	0.39	0.24	0.18	2.1	1.9	2.1	0.52	0.36	0.44
5(10)	0.19	0.20	0.14	2.9	1.8	2.0	0.47	0.42	0.46
5A	0.20	0.20	0.13	2.1	1.7	2.2	0.52	0.50	0.44
5B	0.17	0.20	0.18	2.5	1.2	2.1	0.45	0.61	0.47
5D	0.36	0.13	0.11	2.1	1.4	2.5	0.41	0.47	0.42
5E	0.26	0.20	0.17	2.3	1.5	2.2	0.45	0.51	0.51
5F	0.12	0.20	0.11	2.3	1.5	2.3	0.42	0.44	0.43
5G	0.25	0.18	0.21	2.5	2.0	2.2	0.47	0.43	0.44
5H	-	0.21	0.14	-	2.0	2.2	-	0.40	0.37
6A	0.29	0.12	0.13	2.5	1.7	2.6	0.49	0.50	0.48
6B	0.18	0.11	0.14	2.1	1.8	1.9	0.51	0.55	0.61
6C	0.30	0.11	0.16	2.2	1.9	2.2	0.47	0.51	0.47
6D	0.48	0.14	0.14	2.5	1.6	2.1	0.47	0.55	0.49
6F	0.19	0.18	0.14	2.4	1.9	1.9	0.46	0.45	0.54
6G	-	0.13	0.10	-	2.0	1.2	-	0.39	0.57
7A	0.23	0.15	0.09	2.6	2.0	1.9	0.55	0.54	0.51
7B	0.32	0.19	0.13	2.7	2.3	1.9	0.45	0.43	0.50
7C	0.23	0.14	0.14	2.2	2.1	2.2	0.47	0.44	0.47
7D	-	0.15	0.14	-	2.4	2.4	-	0.46	0.46
7E	0.22	0.16	0.15	3.5	3.6	2.8	0.62	0.61	0.60
7G	0.26	0.25	0.13	4.7	4.4	3.3	0.92	0.74	0.73

[a] Values represent station means

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These compounds had been noted as important features of the Year-1 sediments from this region.

The saturated hydrocarbon composition is shown more clearly in Table 7.17, in which the key diagnostic saturated hydrocarbon parameters are presented. Although the LALK/TALK ratio appears to be relatively constant in the entire Year-1 data set, there is a distinct shift in the composition in East Harrison Bay due to a "depletion" of the LALK compounds in Years-2 and 3. This shift is comparable to the one observed in the Camden Bay area. The source that can be postulated as most responsible for the shift to lower LALK/TALK ratios is coastal peat. River sediment LALK/TALK ratios were generally higher than those in peat. It is hypothesized that inputs of the two major sources of observed hydrocarbons to the offshore sediment, peat, and river sediments can, by shifts in the yearly relative amounts input to the sediment, also shift the composition of the sediments. As shown in Table 7.17, the LALK/TALK ratios are remarkably constant throughout the Study Area during Years-2 and 3. Throughout the entire study period, this useful diagnostic ratio varies as follows:

Region	Geometric Mean (lower 95%; upper 95%)
Entire Study Area	0.17 (0.12, 0.23)
Camden Bay Region	0.18 (0.11, 0.30)
Foggy Island Region	0.18 (0.15, 0.23)
Kuparuk River Region	0.16 (0.14, 0.19)
E. Harrison Bay Region	0.15 (0.09, 0.27)
W. Harrison Bay Region	0.16 (0.11, 0.25)
Endicott Region	0.20 (0.18, 0.21)

These values are extremely useful for the application of this ratio to future monitoring studies. However, equally important is the knowledge that, due to natural causes, the ratio can increase dramatically by a factor of two, as observed in East Harrison Bay (the "6" Stations) in Year-1.

Of the other key saturated hydrocarbon ratios examined (Table 7.17), the ISO/ALK ratio was generally invariant between Years 1, 2 and 3. The PRIS/PHY ratio, in general, appeared to decrease slightly throughout the Study Area in Year-2. Note, however, that the significantly elevated PRIS/PHY ratios observed at Stations 7E and 7G in the West Harrison Bay area during Year-1 were also observed in Year-2 and Year-3. Because the peat sample, obtained directly adjacent to these stations, was also enriched in pristane, peat input appeared to be the dominant source in the Harrison Bay area. This hypothesis is further supported by the GC traces from the sediments from Stations 7E and 7B (Figure 7.15). These chromatograms differed from all others in the Study Area by virtue of the distinct "clusters" of branched alkanes and mono-olefins observed eluting

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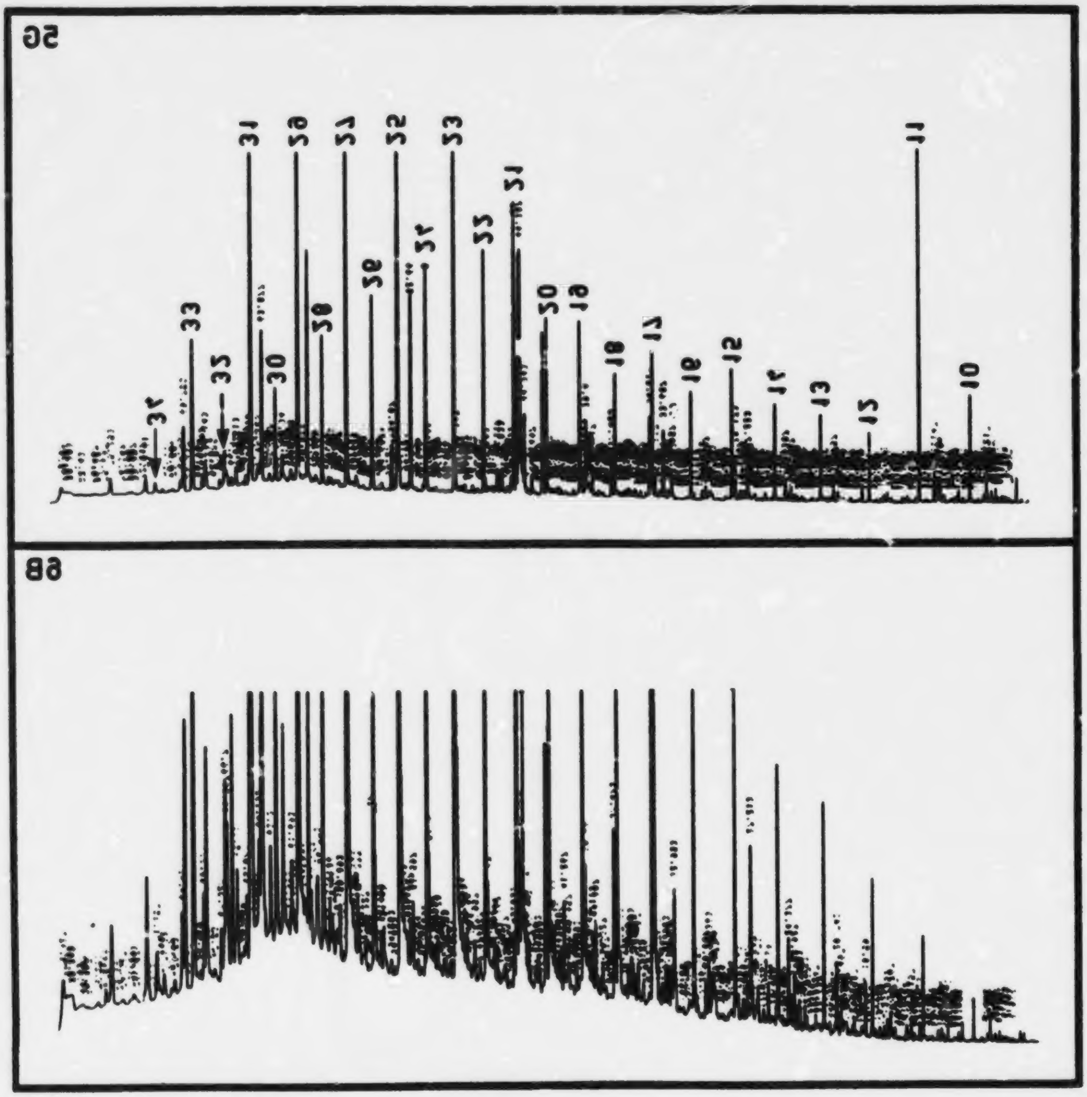

FIGURE 7.14 REPRESENTATIVE FLAME IONIZATION DETECTION GAS CHROMATOGRAMS SHOWING SATURATED HYDROCARBON COMPOSITIONS OF SEDIMENTS AT STATIONS 5G AND 6B

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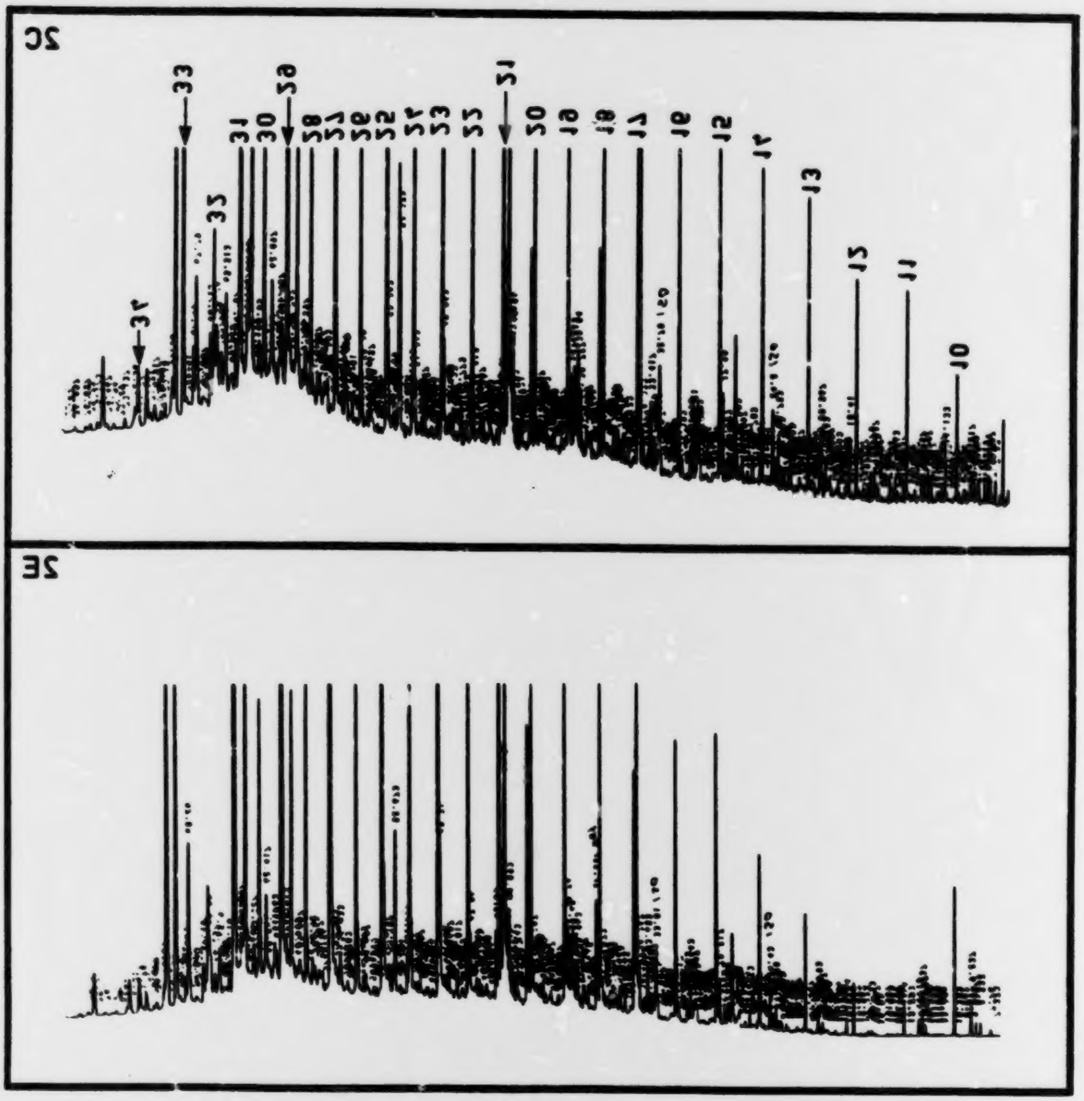

FIGURE 7.13 REPRESENTATIVE FLAME IONIZATION DETECTION GAS CHROMATOGRAMS SHOWING SATURATED HYDROCARBON COMPOSITIONS OF SEDIMENTS AT STATIONS 2C AND 2E

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7.3.3.3 Gas Chromatographic Composition of Saturated Hydrocarbons

The saturated hydrocarbon composition of all surface sediments examined in Year-1 through Year-3, as determined by GC-FID analysis, was composed of two main features: 1) an n-alkane distribution from n-C10 to n-C20, with no odd-carbon dominance (LALK); and 2) an n-alkane distribution from n-C21 to n-C33, with a distinct odd-carbon preference. The total saturated hydrocarbons (TOT), as determined by GC-FID, from all three years are correlated with the TOC content (r = 0.58). The total n-alkanes (TALK), n-C10 to n-C34, are strongly correlated with mud (r = 0.81) and TOC (r = 0.74), and the LALK compounds are less strongly correlated (r = 0.69 for mud; r = 0.63 for TOC). A correlation matrix for all key hydrocarbon and auxiliary parameters is presented in Table 7.16.

Lack of correspondence between TALK and LALK is not unexpected because the two distributions originate in different sources. The higher molecular weight n-alkanes are certainly quantitatively more important than the lower molecular weight compounds. The former originate primarily in waxes from terrigenous higher plants, while the LALK compounds are linked largely to petrogenic inputs. The implied distinctions are clear, although in reality there is considerable overlap in the distributions. Several representative GC-FID traces are presented in Figures 7.12 through 7.14. The chromatogram from Station 6B (Year-1) near the Colville River (Figure 7.14) is of particular interest. At this station, the LALK compounds were of greater relative importance, perhaps due to a relatively high degree of input of petrogenic compounds from the river to the offshore area in Year-1. In subsequent years, the relative inputs at stations near the Colville River and at all other stations in the Study Area were quite similar. As discussed in Section 8, the river inputs contribute the LALK compounds to the offshore sediments, and the coastal peat deposits and the peat content along the river banks contribute primarily the higher molecular weight n-alkanes to the offshore sediments. As the mouth of the Canning River is approached (Station 2C, Figure 7.13) and as the distance offshore increases (Station 1C, Figure 7.12), the LALK compounds appear in greater abundance in the sediments.

Other GC traces from Stations 5G and 6B, shown in Figure 7.14, represent typical sediments from the region; LALK and the higher molecular weight alkanes are found in mixed distribution. Several interesting observations were made in the GC traces from stations in East Harrison Bay (Region 6). Although these sediments contained some of the highest hydrocarbon concentrations found in the Study Area, some of the sediments from Region 6 (Figure 5.5, Station 6D) were surprisingly depleted in the LALK compounds in the Year-2 and Year-3 samples.

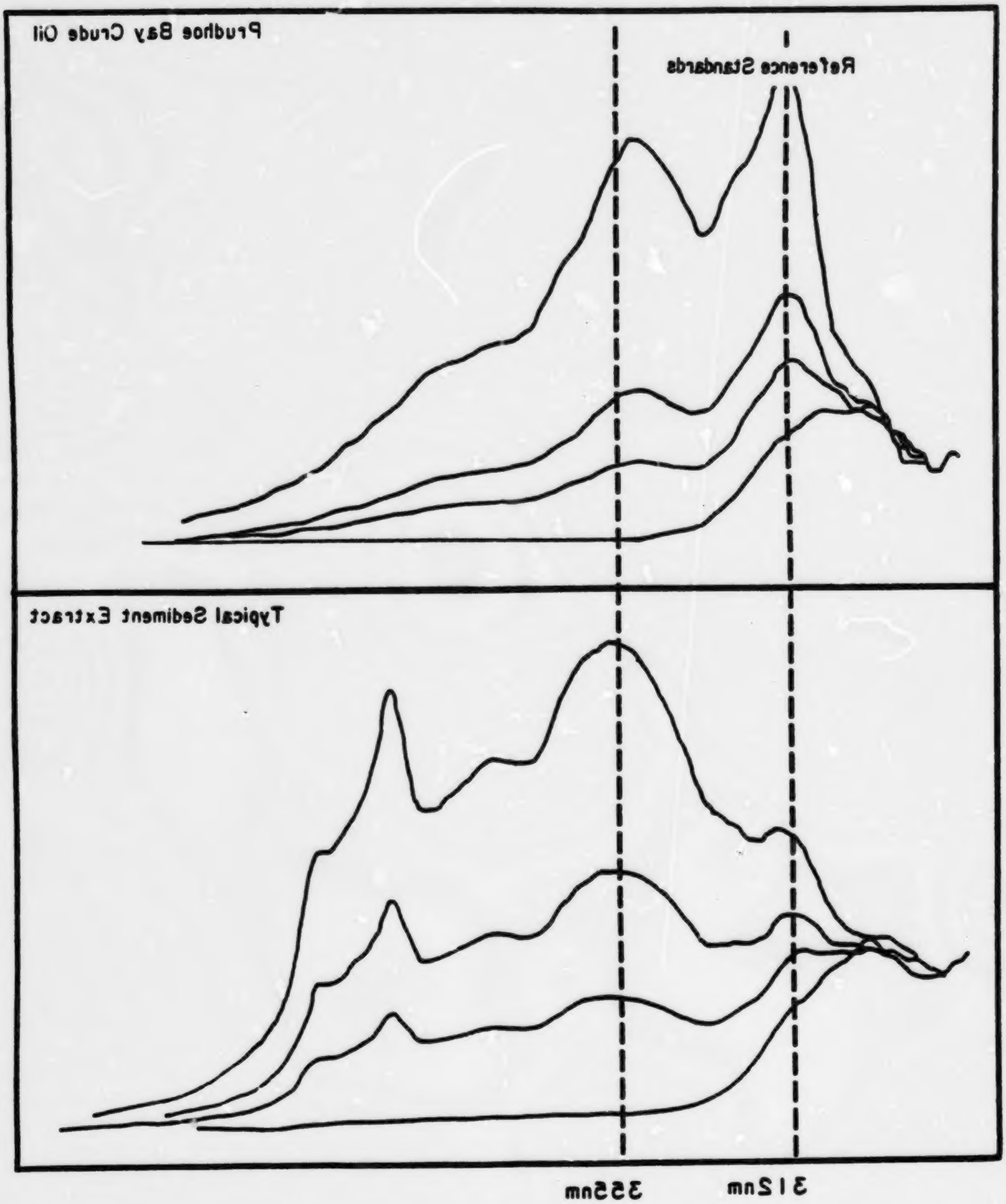

FIGURE 7.11 TYPICAL UV/F SPECTRA OF PRUDHOE BAY CRUDE OIL REFERENCE STANDARD AND TYPICAL SEDIMENT EXTRACT.

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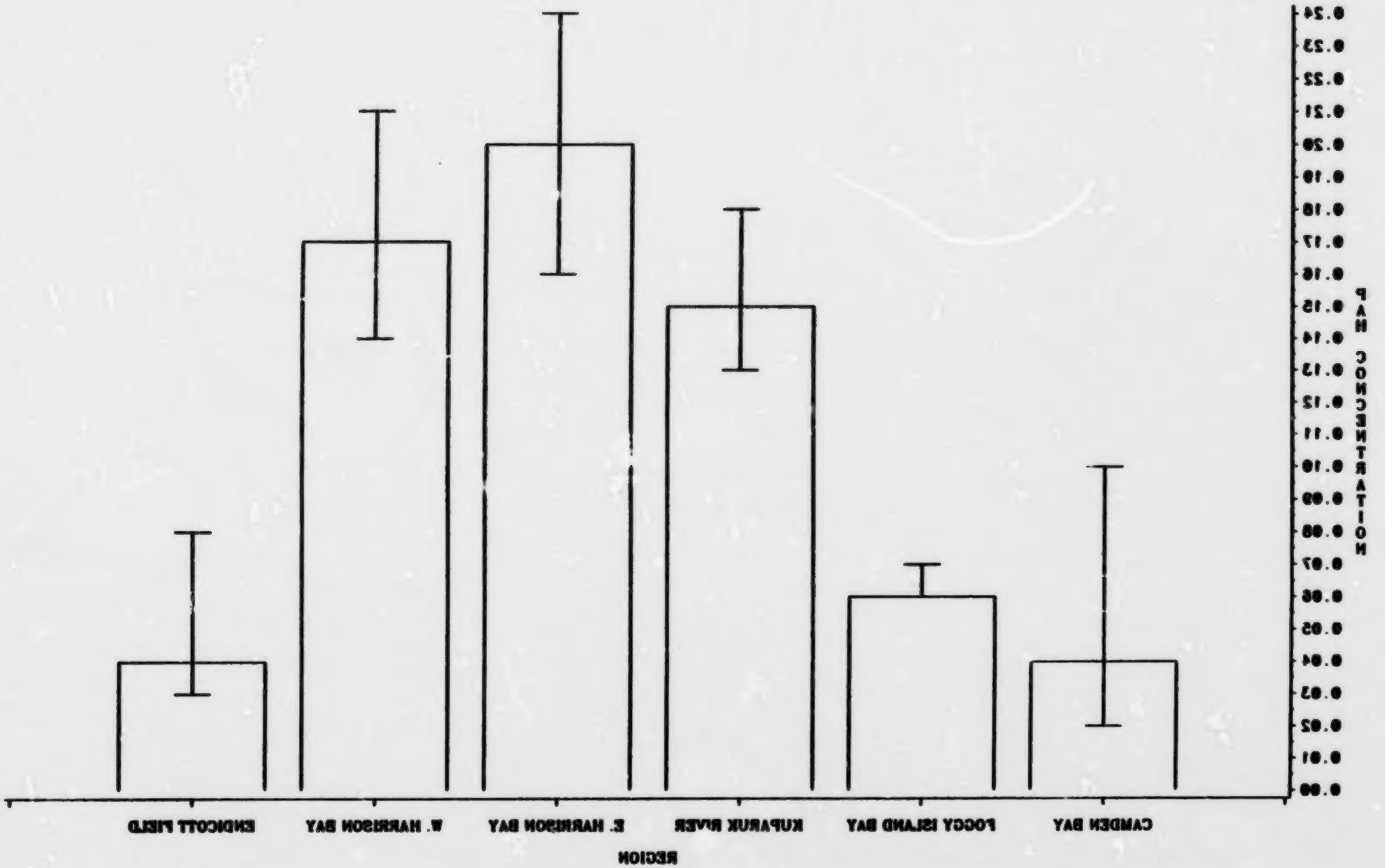

FIGURE 7.10 THREE-YEAR GEOMETRIC MEAN TOTAL PAH CONCENTRATIONS (BRACKETS INDICATE 95 PERCENT CONFIDENCE LIMITS)

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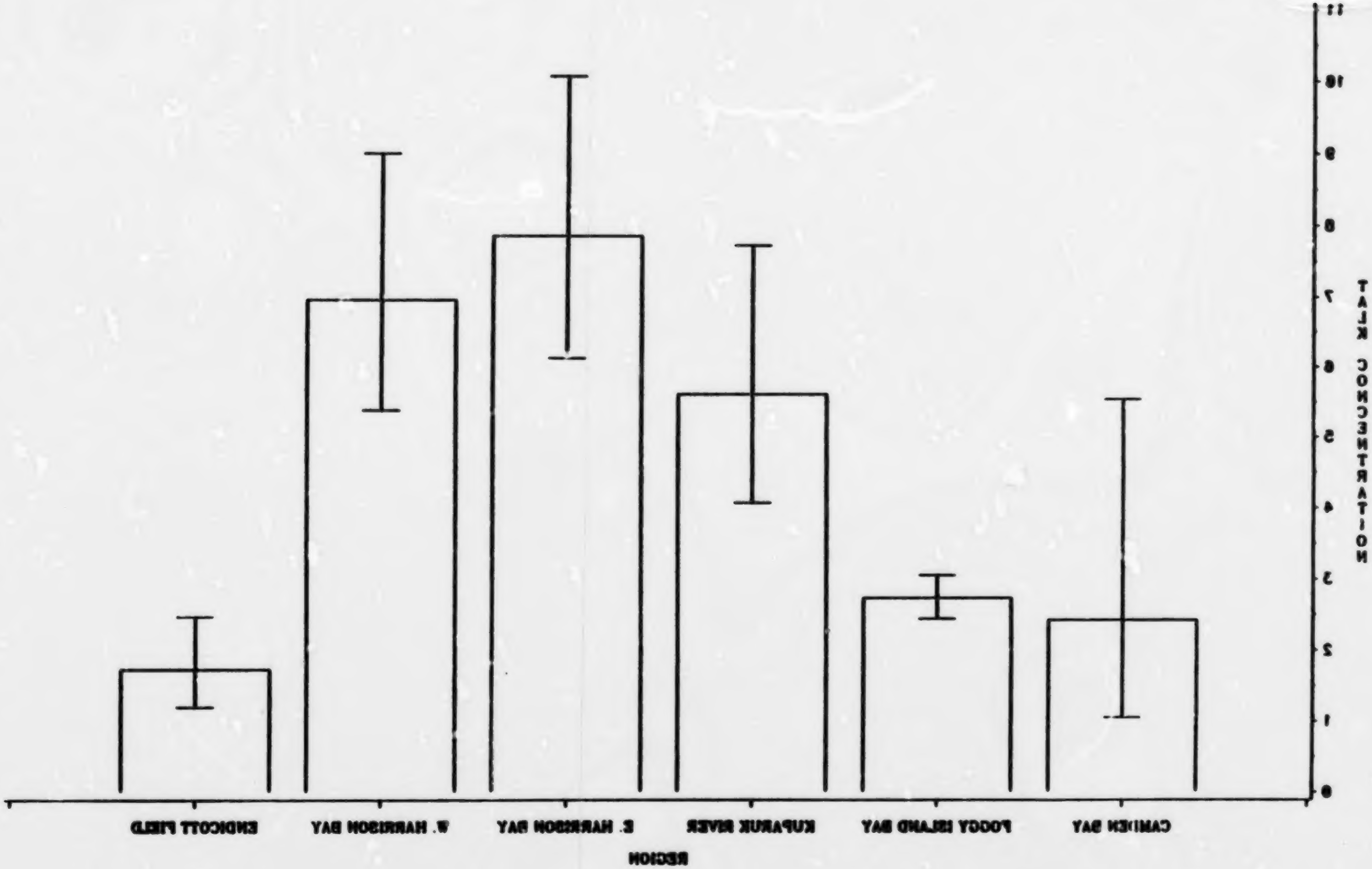

FIGURE 7.9 THREE-YEAR GEOMETRIC MEAN TOTAL ALKANE (TALK) CONCENTRATIONS
(BRACKETS INDICATE 95 PERCENT CONFIDENCE LIMITS)

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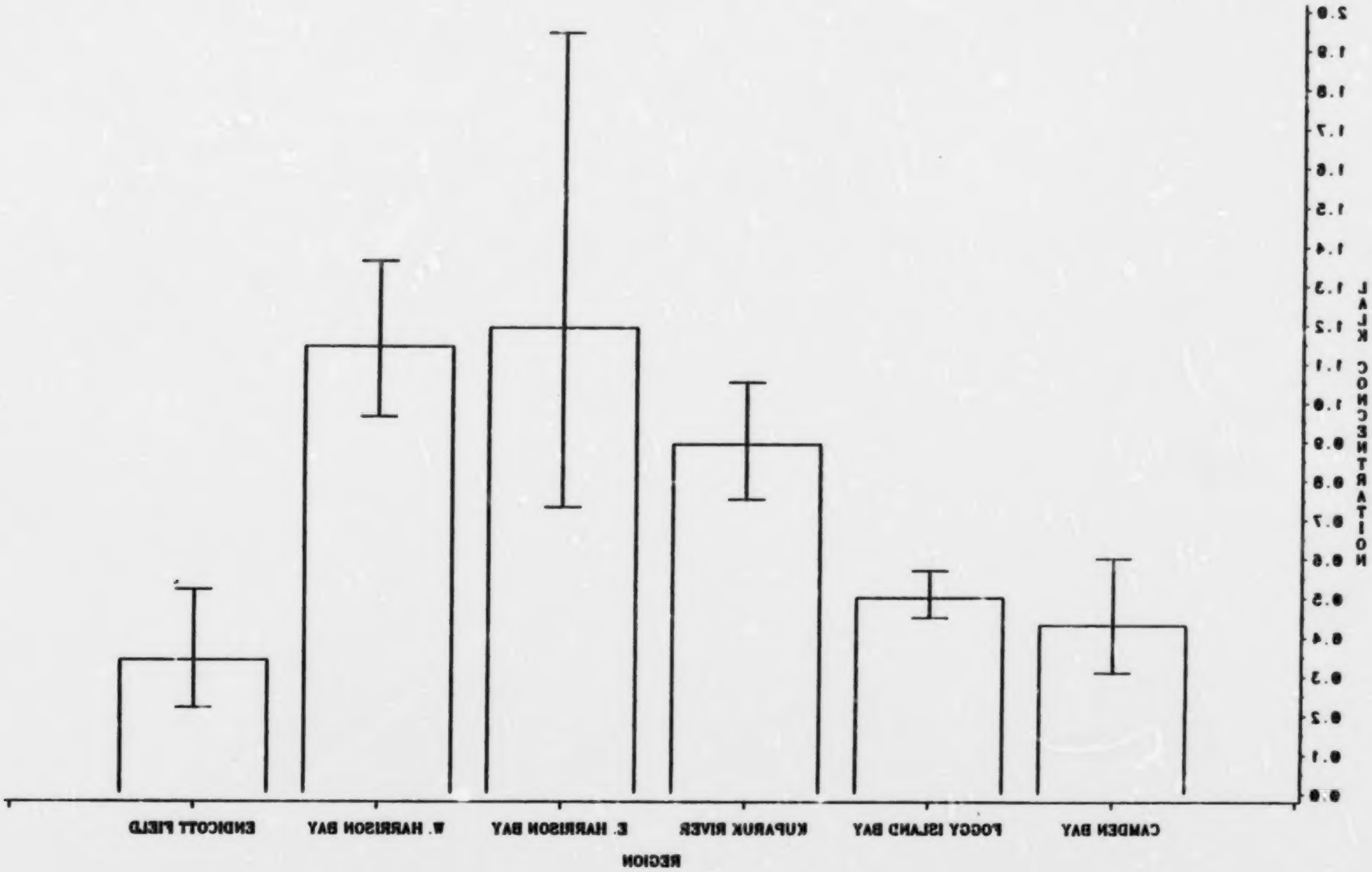

FIGURE 7.8 THREE-YEAR GEOMETRIC MEAN LOW MOLECULAR WEIGHT ALKANE (LALK) CONCENTRATIONS (BRACKETS INDICATE 95 PERCENT CONFIDENCE LIMITS)

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sediment distributions. Two likely sources are coastal peat, which is widespread along the entire coastline of the Beaufort Sea, and riverine sediments. Eight samples of peat were collected from Stations 1F, 2G, 2H, 3D, 5K, 6J, 7H and 7J in Year-2, and two river sediment samples, one each from the Colville and Sagavanirktok Rivers (Stations 6H and 5J, respectfully), were obtained in Year-2. The Year-3 program focused more intensely on sampling river stations from the Canning (Station 2H), Kuparuk (Station 5M), Sagavanirktok (Station 5L), and Colville (Station 6K) Rivers. The hydrocarbon results were previously presented in Section 6. The average values of key saturated hydrocarbon parameters and parameter ratios are presented in Table 7.22. The ratio of total saturates (TOT) to total organic carbon (TOC) in peat averaged 0.027 ± 0.020 over the entire Study Area and ranged from a low of 0.007 at Station 3D (Tigvariak Island) to 0.058 at Station 7J (Kogru Island). The hydrocarbon concentrations in peat were generally much greater than in offshore sediment, but the ratio of TOT/TOC was similar in both sample types. The TOT/TOC ratio in offshore sediments averaged 0.015 and ranged from 0.004 to 0.049.

In examining the data in Table 7.22 for clues as to the relative importance of peat versus river sediment in contributing to the offshore sediment hydrocarbon content, one is directed not to the absolute concentration data, but to the diagnostic ratios LALK/TALK, PRIS/PHY, ISO/ALK and TOT/TOC. The TOT/TOC ratio in peat averaged 0.027, much higher than that in the river sediments (0.112); offshore sediments averaged between the two potential source types. However, the ISO/ALK and, in particular, the LALK/TALK ratios were similar in offshore and river sediments, and quite different from the peat samples. The GC traces of the source types in comparison to each other and to the offshore sediments reveal much about the relative importance of peat and river sediment. Typically, the saturated hydrocarbon distribution in peat is composed of 1) an abundance of terrigenous plant wax n-alkanes (n-C21 to n-C33) with an odd-carbon predominance (OEPI = 7 to 14), and 2) a distinct series of mono-olefins that elute just prior to the corresponding n-alkanes. This mono-olefinic distribution has been reported in lake sediments (Giger et al., 1980) and appears to be associated with organic matter in a state of early diagenesis. These high molecular weight mono-olefins are absent or found at trace concentrations in the offshore sediments. The GC traces in Figure 7.21 also show a general absence of the LALK compounds, an abundance of higher molecular weight alkanes and mono-olefins, and clusters of branched alkanes and mono-olefins eluting around n-C13, n-C15 and n-C17 (Flaxman Island peat sample). This latter distribution was also found in several species of marine animals in the region.

In contrast, the river sediments (Figure 7.22) combined the above-described peat distribution with the abundance of the LALK soil, but rather contains various depths of seasonally thawed peat-like material.

Consequently, the organic matter carried by the Colville River includes fractions derived from peat, coal and oil. Additional peat enters the marine environment from direct erosion of low bluffs that are a common feature on the Beaufort coast. Although these natural sources may account for the PAH found in Harrison Bay sediments, anthropogenic sources associated with river sediments appear to contribute to LALK and the PAH content of the sediment. Suspended material discharged by the Colville moves west following the general coastline of Harrison Bay, as can be seen in satellite photos of the Colville sediment plume (see Naidu et al., 1984). Material can be deposited in shallow water, resuspended, and finally deposited in deeper water. This sediment transport pathway is consistent with the high concentrations in Harrison Bay stations which, compared to other stations, are elevated in all saturated and aromatic compounds.

The high mud (silt + clay) content of Harrison Bay sediments, the sediments of Stations 1A, 1C, 1E, 2A, 2C, and 2E in Camden Bay and at other stations in the Study Area (3B, 5B, 5D) suggest that these regions are the most likely depositional areas of fine-grained particles, low density organic detritus, and anthropogenic inputs.

Two stations (7E and 7G) within Harrison Bay exhibited anomalous biogenic inputs as reflected in higher absolute and relative quantities of pristane. These stations may be the site of elevated productivity, perhaps due to nutrient loadings from the Colville River, or they may be receiving large quantities of pristane-enriched peat originating from Kogru Island and adjacent areas. Marine sediments collected between the mouths of the Colville and Canning Rivers, including the Prudhoe Bay area, showed generally lower total hydrocarbon values than those collected from Harrison Bay. Higher hydrocarbon concentrations are generally associated with finer-grained (3B, 5B, 5D) and more organic-rich (4A, 5A, 5D, 5H) stations. There are probably fewer natural petroleum seeps and coal outcrops to the east of the Canning River. The drainage system east of the Colville River consists of smaller rivers that discharge material more uniformly along the coast but, nevertheless, contain anthropogenic materials as found in the Sagavanirktok River. These factors will lead to greater dispersion and lower concentrations of background hydrocarbon distributions.

7.3.4 River and Peat

Due to the abundance of trace metals and saturated hydrocarbons and the high PAH content observed in sediments sampled in Year-1, the Year-2 and Year-3 programs focused partly on examining possible source materials for observed offshore

TABLE 7.21 COMPARISON OF BULK SEDIMENT AND MUD FRACTION ANALYTICAL RESULTS FOR AROMATIC HYDROCARBON PARAMETERS AND RATIOS

Station	ΣPAH^a	FFPI	N/P	P/D	% Mud
1A					
Bulk	0.26	0.61	1.0	5.9	69
Mud	0.60	0.60	1.1	5.8	
5(5)					
Bulk	0.14	0.69	0.9	6.2	23
Mud	1.0	0.68	1.3	8.3	
6D					
Bulk	0.39	0.73	1.4	4.9	18
Mud	2.1	0.70	1.4	7.0	

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TABLE 7.20 THREE-YEAR SUMMARY OF KEY AROMATIC HYDROCARBON RATIOS FOR THE BEAUFORT SEA STUDY AREA REGIONS[a]

Region	N/P	P/D
Camden Bay	0.8 (0.5, 1.3)	8.2 (6.6, 10.1)
Foggy Island Bay	1.0 (0.9, 1.6)	6.2 (4.0, 9.4)
Kuparuk River Area	1.2 (0.9, 1.6)	4.7 (3.7, 6.1)
Endicott/Prudhoe	1.0 (0.8, 1.2)	5.1 (3.8, 6.7)
E. Harrison Bay	1.5 (1.2, 2.6)	4.6 (4.3, 5.0)
W. Harrison Bay	1.6 (1.3, 1.8)	5.3 (4.2, 6.8)
Entire Study Area	1.2 (1.0, 1.4)	5.6 (4.7, 6.8)

[a] Geometric means (lower 95%, upper 95%)

Study Area regions varied by a factor of two (Table 7.20), with the highest ratio (1.6) associated with sediments from the Harrison Bay region.

With the exception of Camden Bay, the P/D sediment ratios for the other regions are quite similar (Table 7.20). The high P/D ratio for the Camden Bay sediments indicates potentially lower overall natural petrogenic inputs than is observed throughout the other Study Area regions. The distinct differences between these ratios found in sediments (see Table 7.20) and the corresponding ratios found in Prudhoe Bay crude oil (4.0 and 1.1, respectively for N/P and P/D) make these ratios good diagnostic indicators of potential petrogenic inputs. The abundance of the dibenzothiophenes (D) in oil and, specifically, the low ratio of P/D, are excellent potential indicators of petrogenic inputs, with the D compounds present at low absolute and relative quantities in the sediments, and present at larger relative quantities in the crude oil sample.

As with the saturated hydrocarbons, the PAH content and composition was explored in bulk sediments and their corresponding mud fractions in Year-2. The results are summarized in Table 7.21. The key diagnostic parameter ratios of FFPI, N/P and P/D were very similar in the bulk and mud fractions, in spite of large absolute concentration differences in the PAH content.

7.3.3.5 Statistical Correlations

In order to view the individual saturated and aromatic hydrocarbon parameters on a more regional basis, Pearson correlation coefficients were computed for the major parameters. This correlation matrix is presented in Table 7.16.

7.3.3.6 Geographic Analysis

The distribution of hydrocarbons in Harrison Bay can be understood in terms of input from the Colville River and the general east-to-west flow in the coastal Alaskan Beaufort Sea. The Colville, although smaller than the MacKenzie River in Canada, is the largest Alaskan river emptying into the Beaufort Sea. The Colville drains most slopes of the Brooks Range (but not the coastal plain) between 150° and 160°W; the annual flow is estimated at 100 billion cubic meters, with an average TOC content of 12 mg/L. The region drained by the Colville River contains numerous outcropping coal deposits, as well as natural petroleum-seep areas and oil-shale outcrops. In particular, there is a 1.5-mile-long Oil Lake (70° 18'N; 151°09'W) slightly west of the Colville and 5 miles from the coast. This lake was named for the natural seep oil that forms a slick on its surface. The terrain drained by the Colville, like the terrain of the entire Alaskan north slope, does not have well-developed

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TABLE 7.19 SUMMARY OF SEVERAL KEY AROMATIC HYDROCARBON DIAGNOSTIC RATIOS FOR SEDIMENTS AT ALL MARINE STATIONS

Station	FFPI			N/P			P/D		
	Yr-1	Yr-2	Yr-3	Yr-1	Yr-2	Yr-3	Yr-1	Yr-2	Yr-3
1A	-	0.61	0.78	-	0.99	1.3	-	5.9	7.3
1B	-	0.71	0.75	-	1.1	0.83	-	5.8	5.8
1C	-	0.68	0.60	-	1.2	1.4	-	4.8	14
1D	-	0.61	0.85	-	1.4	1.3	-	14	17
1E	-	0.71	0.82	-	1.1	0.93	-	14	4.2
2A	-	0.72	0.73	-	0.81	0.85	-	9.0	6.9
2B	-	0.69	0.73	-	1.0	1.1	-	8.1	6.3
2C	-	0.69	0.77	-	1.3	1.4	-	4.7	3.5
2D	-	0.70	0.79	-	2.8	1.2	-	5.1	6.4
2E	0.85	0.79	0.68	0.59	1.3	0.79	7.9	7.8	8.1
2F	0.76	0.82	0.87	0.46	0.96	0.73	13	35	10
3A	0.81	0.75	0.78	0.79	1.2	1.3	8.6	11	4.6
3B	0.84	0.79	0.76	0.92	0.57	1.2	8.4	7.1	4.3
4A	0.82	0.80	0.82	0.93	1.2	0.94	4.5	11	3.7
4B	0.87	0.74	0.77	1.0	1.1	1.6	3.4	11	4.0
4C	0.82	0.73	0.73	0.74	1.1	1.2	4.5	10	3.7
5(0)	-	0.65	0.80	-	1.0	1.2	-	8.8	4.1
5(1)	0.83	0.69	0.77	0.79	0.90	1.1	5.1	12	2.7
5(5)	0.76	0.69	0.88	0.74	0.93	1.3	5.4	6.2	5.7
5(10)	0.83	0.77	0.67	0.81	1.3	0.93	5.0	3.9	5.0
5A	0.81	0.73	0.77	1.1	1.7	1.6	9.4	6.6	3.5
5B	0.83	0.73	0.86	0.81	1.3	1.4	4.0	5.7	3.5
5D	0.79	0.74	0.79	0.91	1.3	1.5	5.8	4.4	3.2
5E	0.85	0.73	0.75	0.91	1.5	1.1	4.6	5.7	5.8
5F	0.69	0.68	0.78	0.86	1.1	1.6	6.7	3.6	3.5
5G	0.79	0.71	0.67	0.94	1.3	1.3	7.5	14	6.3
5H	-	0.76	0.66	-	1.1	0.92	-	8.1	9.7
6A	0.83	0.77	0.85	0.99	1.5	2.1	3.5	5.2	3.4
6B	0.85	0.83	0.87	1.7	2.3	2.4	6.2	5.0	4.5
6C	0.83	0.76	0.71	0.96	1.5	1.4	4.5	4.6	5.1
6D	0.79	0.74	0.83	1.0	1.3	1.8	5.1	4.9	4.1
6F	0.82	0.81	0.81	1.1	1.6	1.8	5.3	5.4	4.7
6G	-	0.78	0.83	-	1.8	1.6	-	5.4	4.4
7A	0.83	0.76	0.83	1.3	2.0	1.8	5.6	5.5	3.7
7B	0.80	0.77	0.79	1.1	1.7	1.8	4.9	4.7	4.7
7C	0.83	0.89	0.81	1.1	1.7	1.5	5.7	4.4	
7D	-	0.81	0.74	-	0.86	1.5	-	5.4	3.8
7E	0.88	0.81	0.84	1.7	2.0	2.3	7.4	6.0	3.9
7G	0.88	0.80	0.84	1.7	0.88	2.2	12	8.2	6.0
Prudhoe Bay Crude Oil		1.00			4.0			1.1	

Dashes indicate no sample

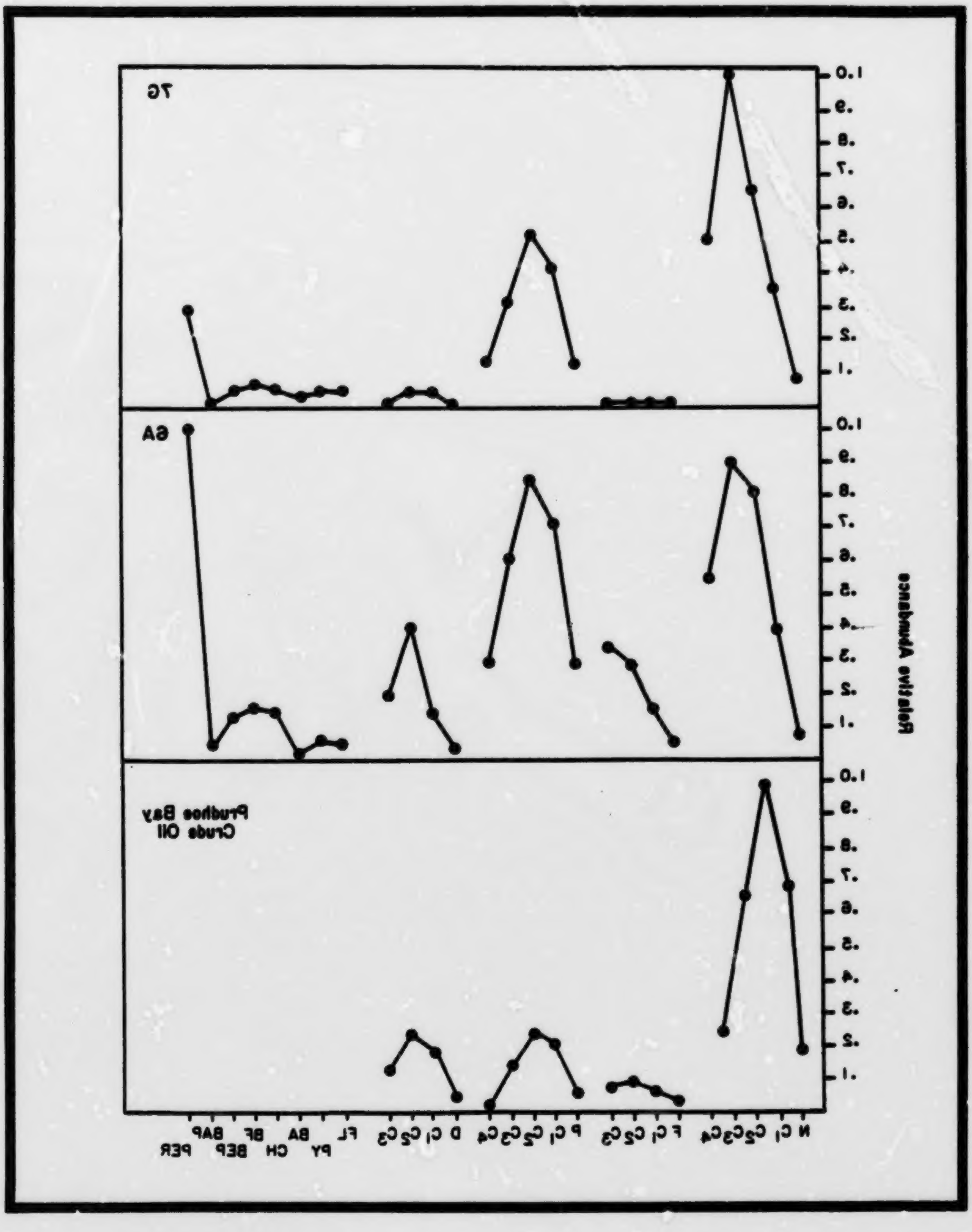

FIGURE 7.20 RELATIVE ABUNDANCE OF AROMATIC HYDROCARBONS FOR REPRESENTATIVE SEDIMENT STATIONS (7G AND 6A) AND FOR PRUDHOE BAY CRUDE OIL

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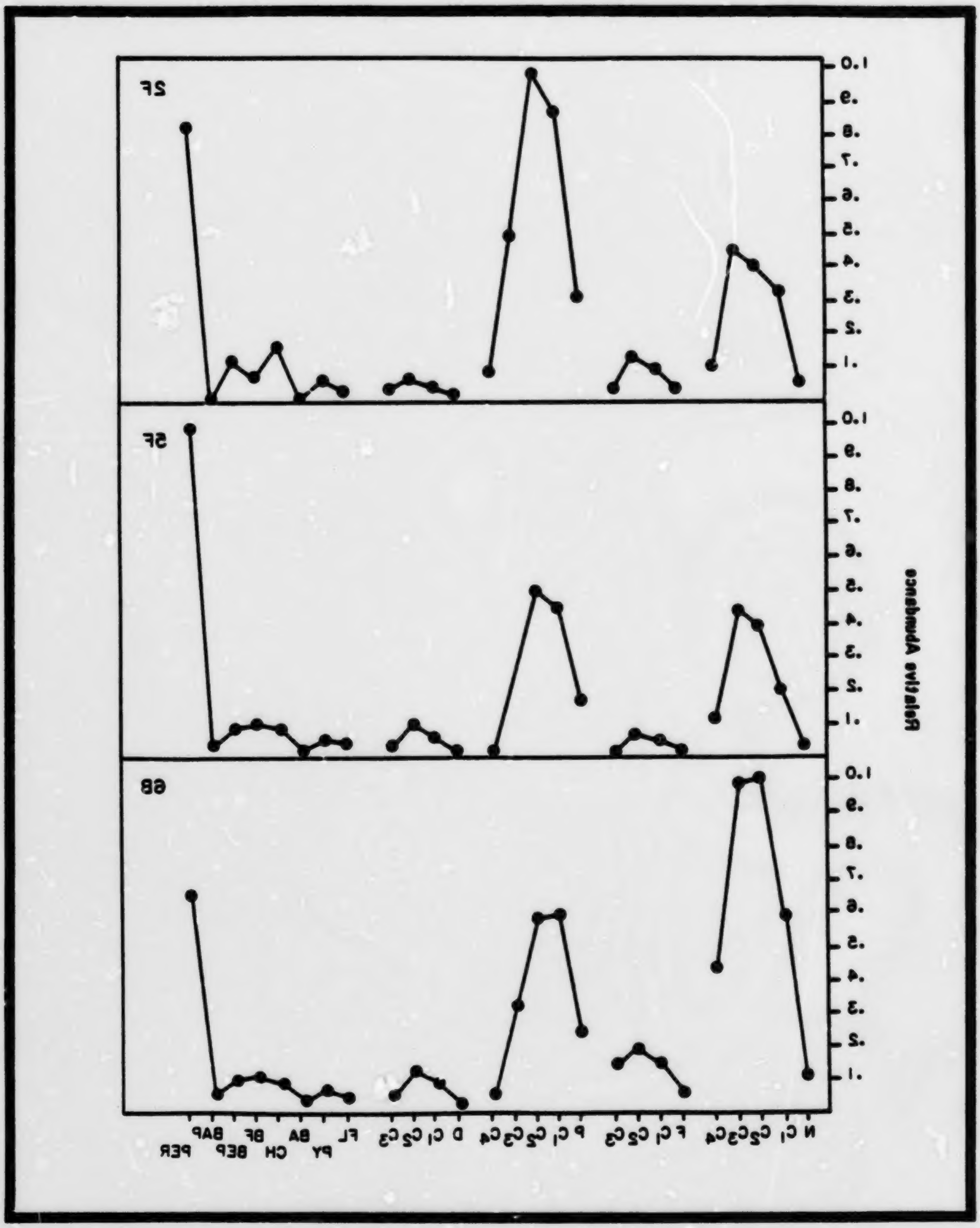

FIGURE 7.19 RELATIVE ABUNDANCE OF AROMATIC HYDROCARBONS FOR REPRESENTATIVE SEDIMENT STATIONS (2F, 5F, AND 6B)

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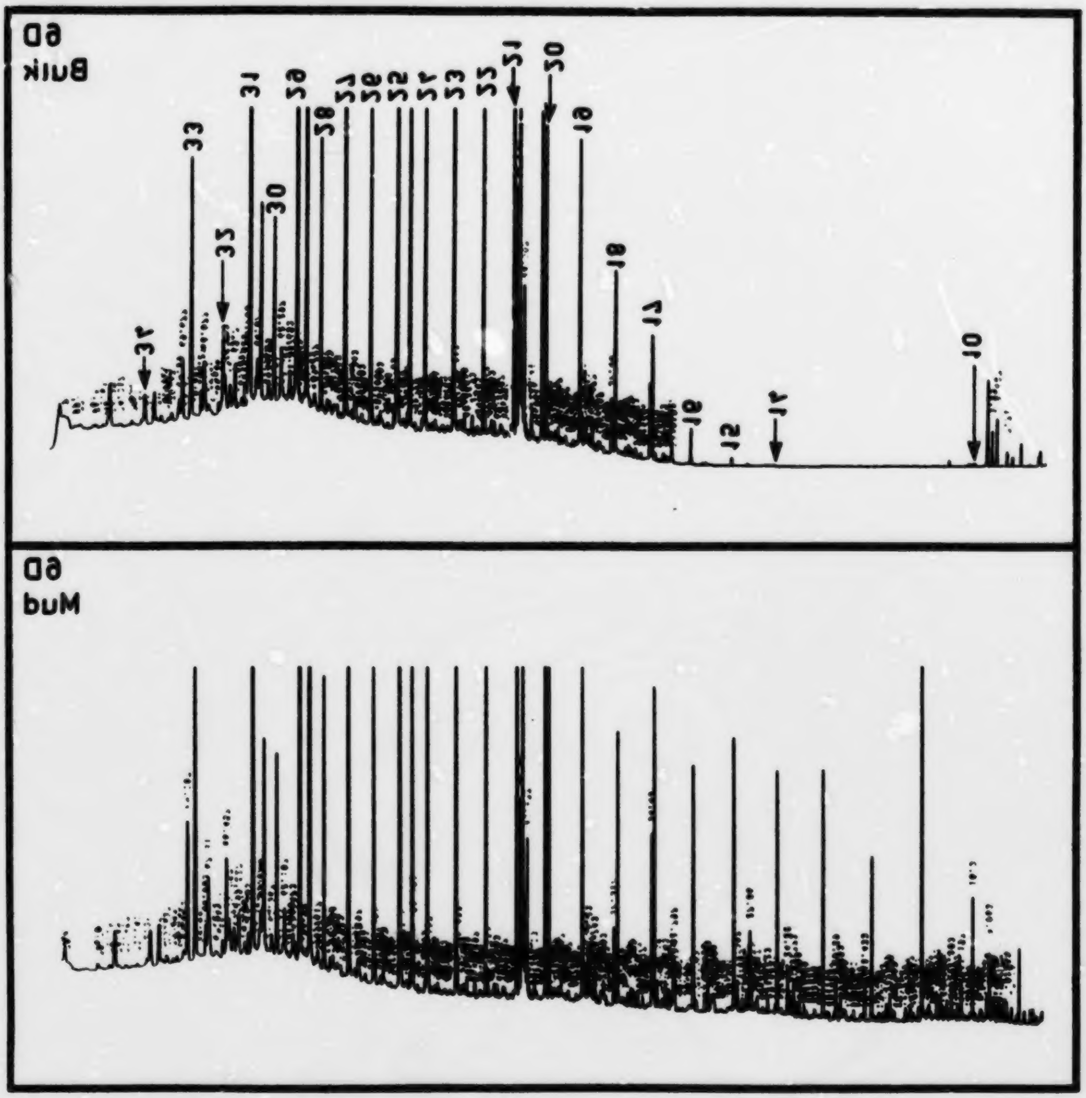

FIGURE 7.18 FLAME IONIZATION DETECTION GAS CHROMATOGRAMS COMPARING SATURATED HYDROCARBON COMPOSITIONS OF BULK SEDIMENT AND MUD FRACTION FROM STATION 6D

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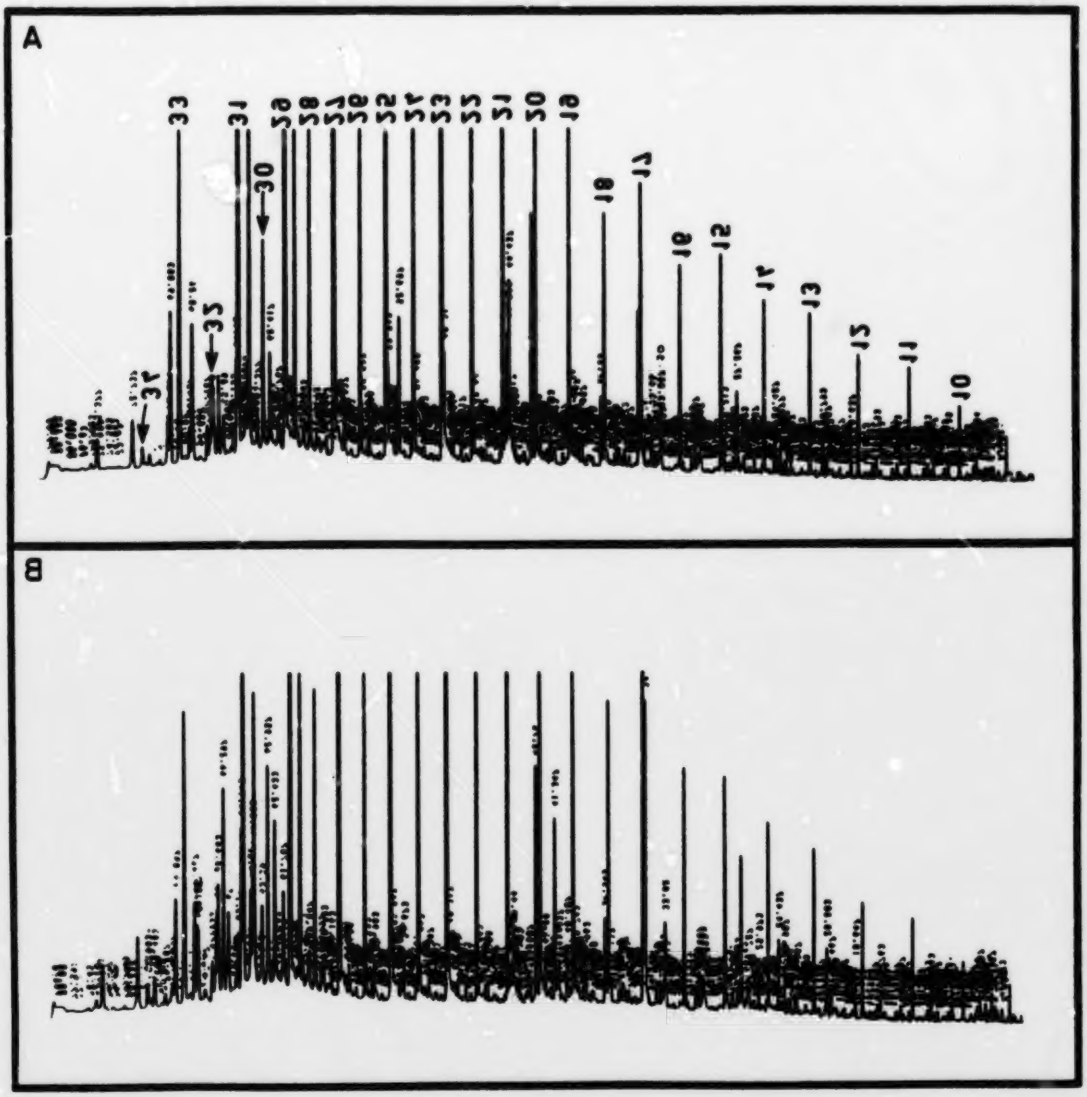

FIGURE 7.17 FLAME IONIZATION DETECTION GAS CHROMATOGRAMS COMPARING SATURATED HYDROCARBON COMPOSITIONS OF BULK SEDIMENT (A) AND MUD FRACTION (B) FROM STATION 7D

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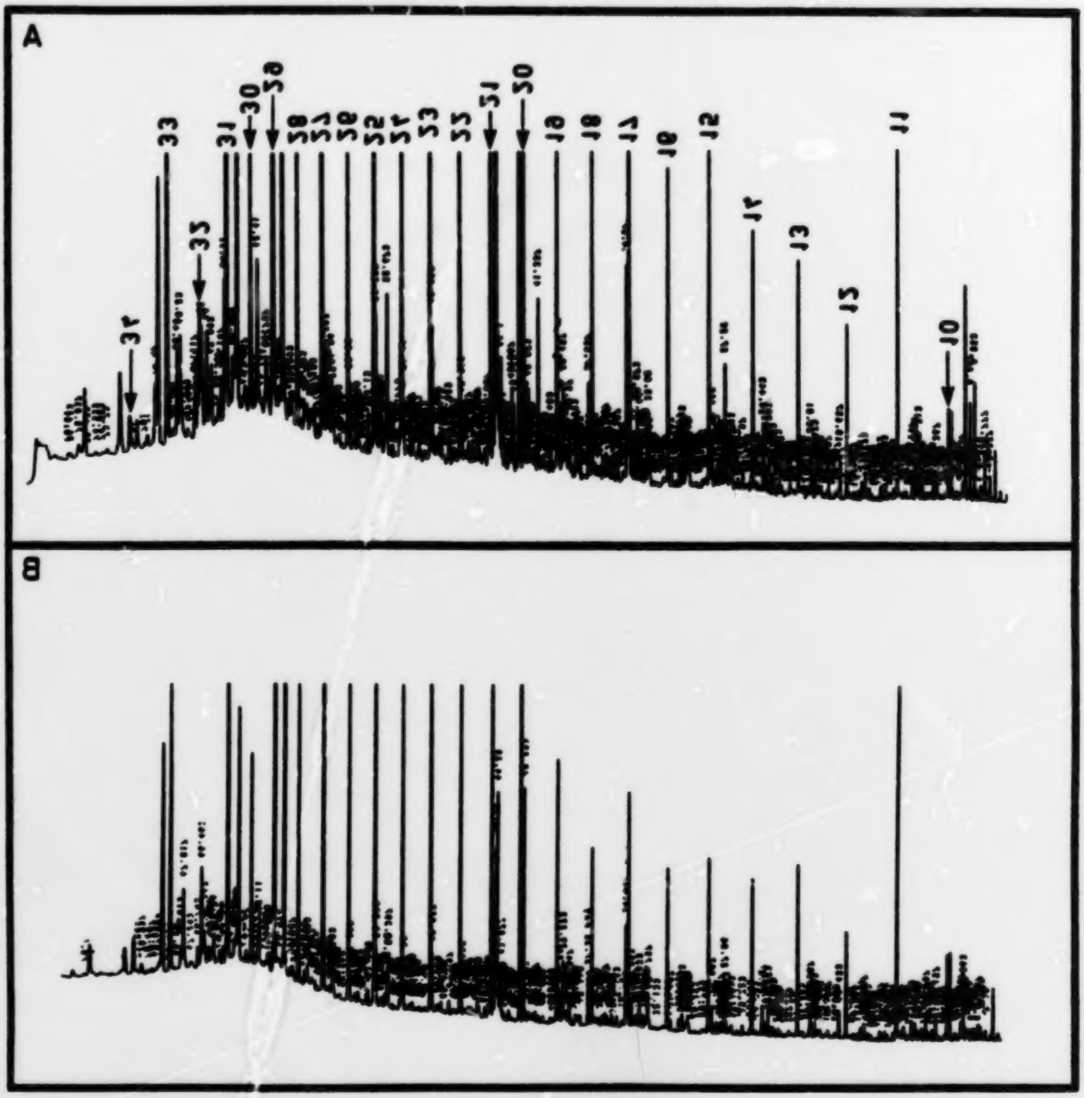

FIGURE 7.16 FLAME IONIZATION DETECTION GAS CHROMATOGRAMS COMPARING SATURATED HYDROCARBON COMPOSITIONS OF BULK SEDIMENT (A) AND MUD FRACTION (B) FROM STATION 5(5)

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TABLE 7.18 COMPARISON OF BULK SEDIMENT AND MUD FRACTION ANALYTICAL RESULTS FOR SATURATED HYDROCARBON PARAMETERS AND RATIOS

Station	LALK (µg/g)	TALK (µg/g)	LALK/TALK	PRIS/PHY	ISO/ALK	TOT (µg/g)	% MUD
1A							
Bulk	0.6	7.5	0.08	1.8	0.38	17	69
Mud	1.3	15.7	0.09	1.5	0.41	27	
5(5)							
Bulk	0.5	2.3	0.20	1.9	0.36	5.3	23
Mud	2.2	12.3	0.18	2.0	0.40	21	
6D							
Bulk	0.3	2.6	0.14	1.6	0.55	7.6	18
Mud	3.8	17.1	0.22	1.8	0.45	35	

near n-C11, n-C13, n-C15 and n-C17. The peat sample from Kogru Island, directly adjacent to these stations, had identical features.

One aspect of the Year-2 hydrocarbon study was a limited examination of the content and composition of bulk sediment and the isolated mud fraction of sediments from three stations. These comparisons (Table 7.18), indicate that the concentration increased by a factor of 2 to 10. When the mud fraction was analyzed separately, this increase was directly related to the mud content of the sediment, and followed from the strong correlation of saturated hydrocarbon and mud content (r = 0.76). However, the values of the key diagnostic saturated hydrocarbon parameters were similar in all bulk and mud fraction pairs, as additionally illustrated by the GC traces in Figures 7.16, 7.17 and 7.18.

7.3.3.4 Aromatic Hydrocarbon Composition

The analytical results on the set of aromatic hydrocarbon (PAH) determinations were presented in Section 6. Throughout the study period, the PAH composition of the sediments was fairly uniform, with the 2- and 3-ring naphthalene and phenanthrene series dominant in most of the sediments. Several typical PAH compositional plots from the Year-1 sediments (Figures 7.19 and 7.20) represent the range of PAH compositions observed in all of the sediments analyzed. The quantity of the naphthalene and phenanthrene homologous series greatly exceeded that of the 4- and 5-ring PAH. This situation confounds the ability to detect increments of oil-derived PAH to the sediments. As discussed in previous annual reports, this situation is highly unusual for coastal marine sediments. In other continental shelf regions not impacted by petroleum pollutants, the 4- and 5-ring PAH compounds usually dominate. As a result of this dominance, the FFPI diagnostic ratios are quite low, typically 0.1 to 0.4 in most unimpacted marine sediments. Thus, with an incremental addition of petrogenic PAH having an FFPI of near unity, the ratio increases and petrogenic inputs can be detected. In the Beaufort Sea sediments, the inputs of river sediments appear to contribute to the lower molecular weight PAH as they contribute to the LALK compounds (discussed above).

Although use of PAH in subsequent monitoring is difficult, the key is to examine details of the PAH assemblage. Several diagnostic ratios are presented in Table 7.19. We have previously found that the more subtle aspects of the PAH composition, namely the N/P and P/D ratios, appear to be potentially more useful for monitoring purposes than the FFPI or the absolute concentration data. Because the more volatile naphthalene compounds are indicative of relatively recent petroleum inputs, the N/P ratio can be an especially useful tool for monitoring. Three-year mean sediment N/P ratios for the

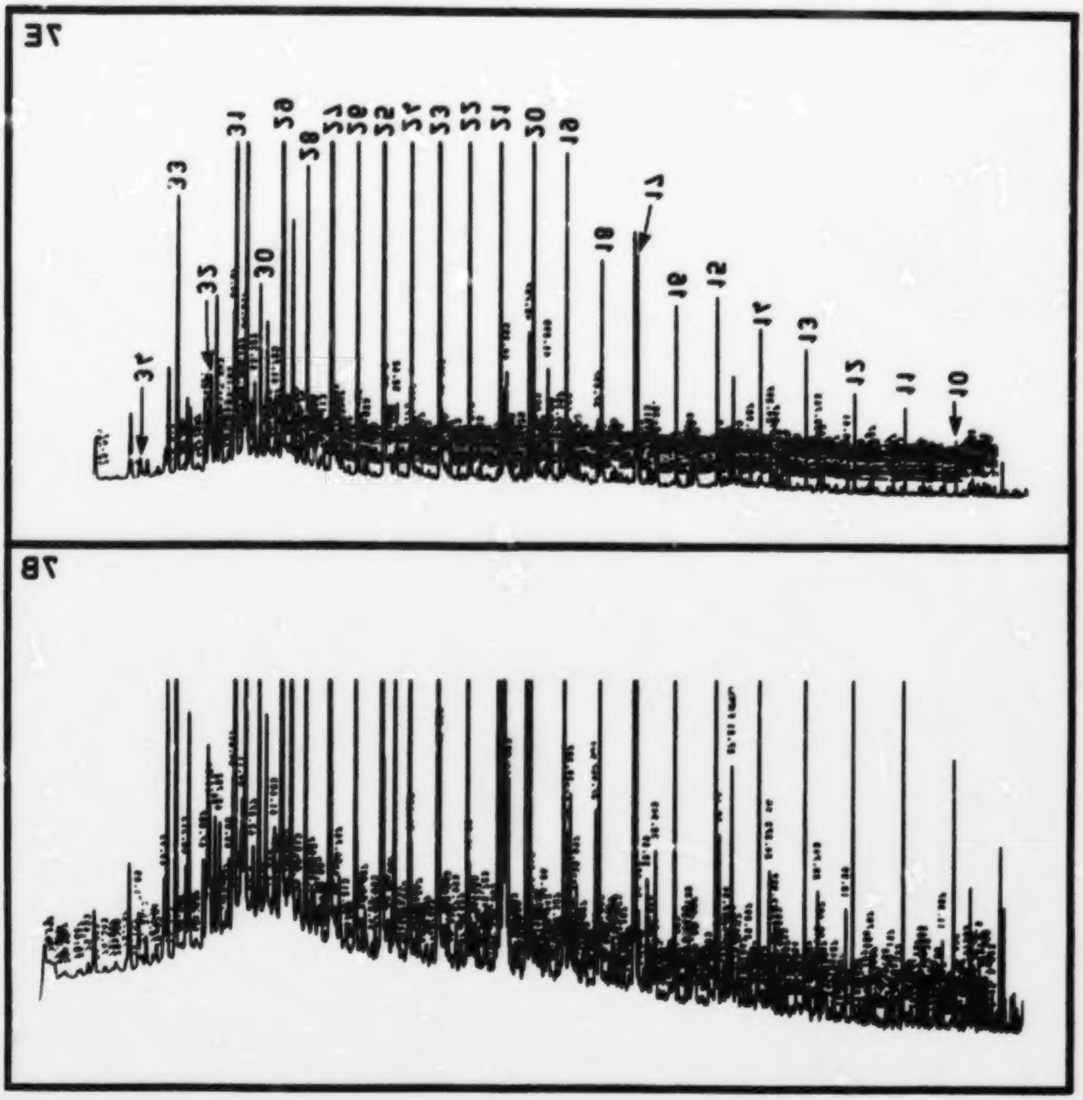

FIGURE 7.15 REPRESENTATIVE FLAME IONIZATION DETECTION GAS CHROMATOGRAMS SHOWING SATURATED HYDROCARBON COMPOSITIONS OF SEDIMENTS AT STATIONS 7E AND 7B

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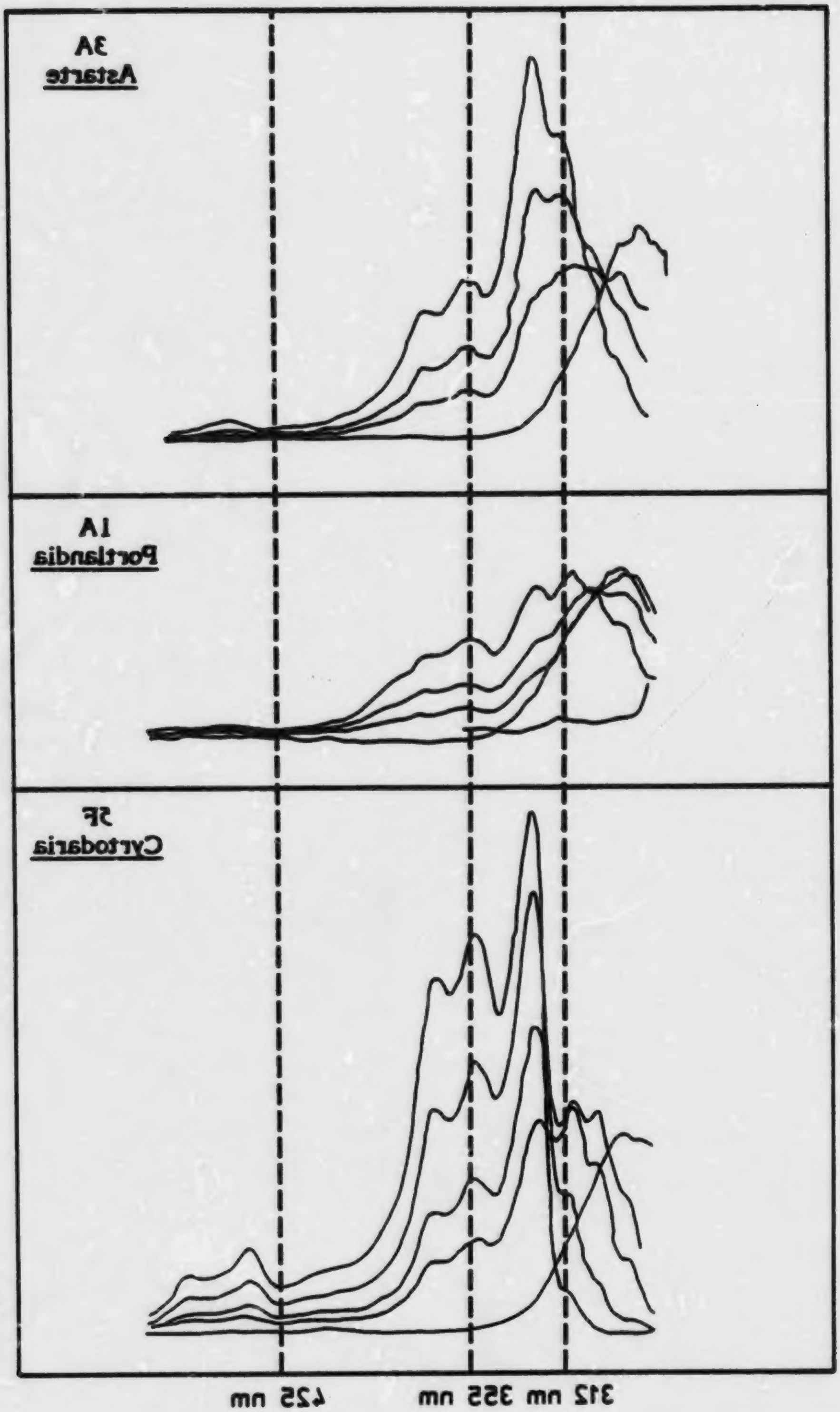

FIGURE 7.29 REPRESENTATIVE UV/F SPECTRA OF ASTARTE, PORTLANDIA, AND CYRTODARIA

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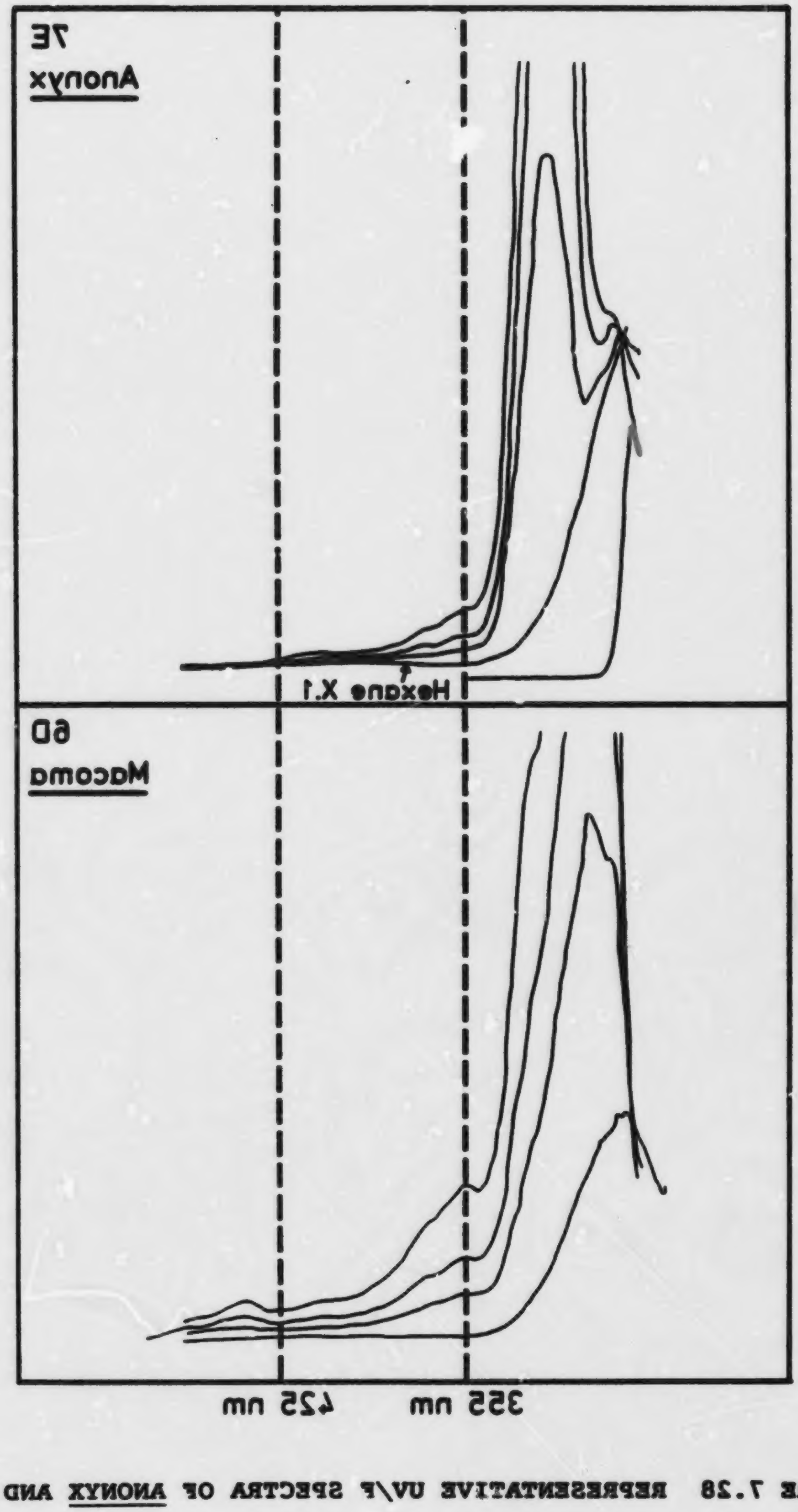

FIGURE 7.28 REPRESENTATIVE UV/F SPECTRA OF ANONYX AND MACOMA

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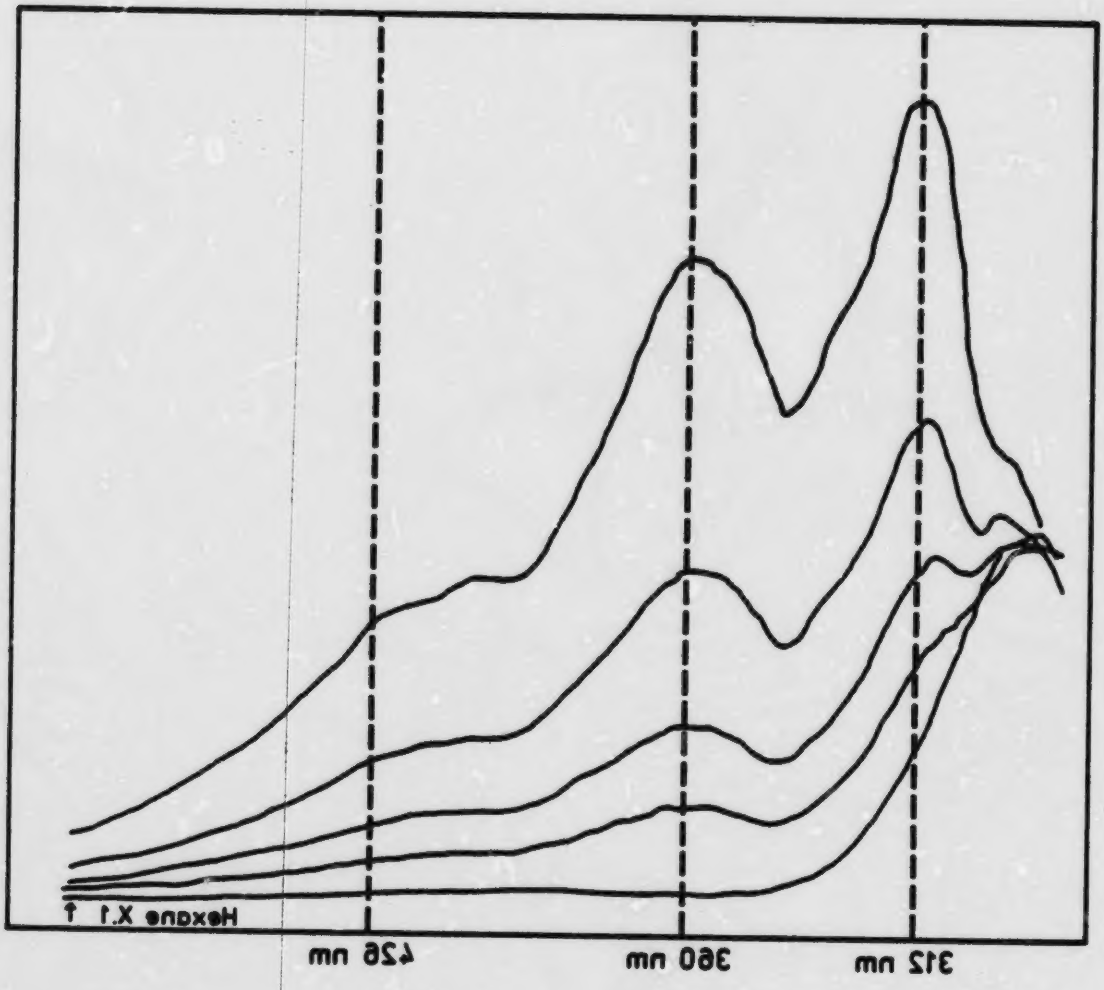

FIGURE 7.27 UV/F SPECTRUM OF STANDARD PRUDHOE BAY CRUDE OIL

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offshore Year-1 sediments (Figures 7.19 and 7.20), the similarity of river and offshore sediments was again apparent.

7.3.5 Tissue Hydrocarbons

The tissue hydrocarbon data obtained in the Year-2 and Year-3 programs represented more extensive sets of data than obtained in Year-1: more species were obtained, a larger area was covered, and more samples were collected. Thus, the Year-2 data should really be considered the initial data set for trend analyses and hypothesis testing. Efforts were made in Year-3 to specifically repeat the Year-2 tissue analytical effort. The samples obtained in Years 2 and 3 were as follows:

- Year-2 Bivalves:
  - *Astarte borealis* - Stations 1B, 3A, 5H, 6D
  - *Cyrtodaria kurriana* - Stations 5F and 6G
  - *Portlandia arctica* - Station 1A
  - *Macoma calcarea* - Station 6D
- Year-2 Amphipods:
  - *Anonyx* sp. - Stations 1A, 1B, 1E, 4B, 5H, 6G, 7B/7C, and 7E.
- Year-3 Bivalves:
  - *Astarte borealis* - Stations 1A, 1B, 2F, 3A, 5H, 5(1), 6D
  - *Cyrtodaria kurriana* - Stations 5F, 6G
  - *Portlandia arctica* - Station 1A
- Year-3 Amphipods:
  - *Anonyx* sp. - Stations 1A, 1B, 7B, 7C, 7E

Amphipod samples from some stations were pooled in Year-2 as indicated to yield sufficient tissue for the analysis of two to four replicates. Where sufficient biomass was available from a single station, four replicates were analyzed.

The species collected for tissue analysis represented two basic feeding types: those that filter seawater and potentially acquire anthropogenic chemical contaminants from the water column (*Astarte*, *Cyrtodaria*), and those that could acquire such chemicals through processing of detritus at the sediment-water interface (*Anonyx*, *Macoma*, *Portlandia*). Replicate analyses were performed using UV/F, GC, and GC/MS techniques.

The UV/F analyses provide important information on the fluorescent material (presumably aromatic in nature) at each of three wavelengths corresponding to spectral maxima in a standard Prudhoe Bay crude oil sample (Figure 7.27). Examples of the character of the UV/F spectra for each species for selected Year-2 samples are presented in Figures 7.28 and 7.29. Several distinct consistent spectral patterns were revealed. *Anonyx*

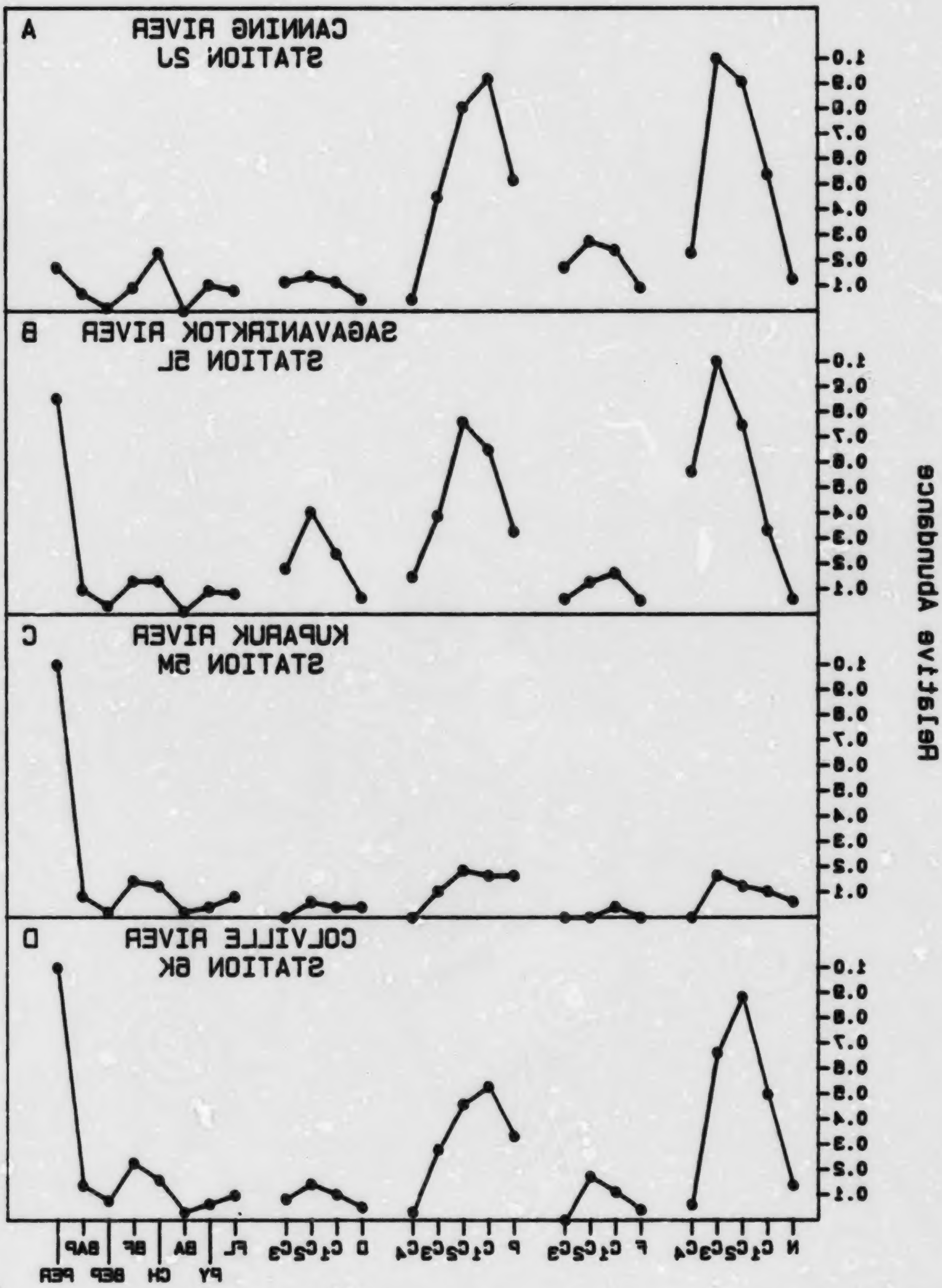

FIGURE 7.26 RELATIVE ABUNDANCE OF AROMATIC HYDROCARBONS IN YEAR-3 RIVER SEDIMENTS

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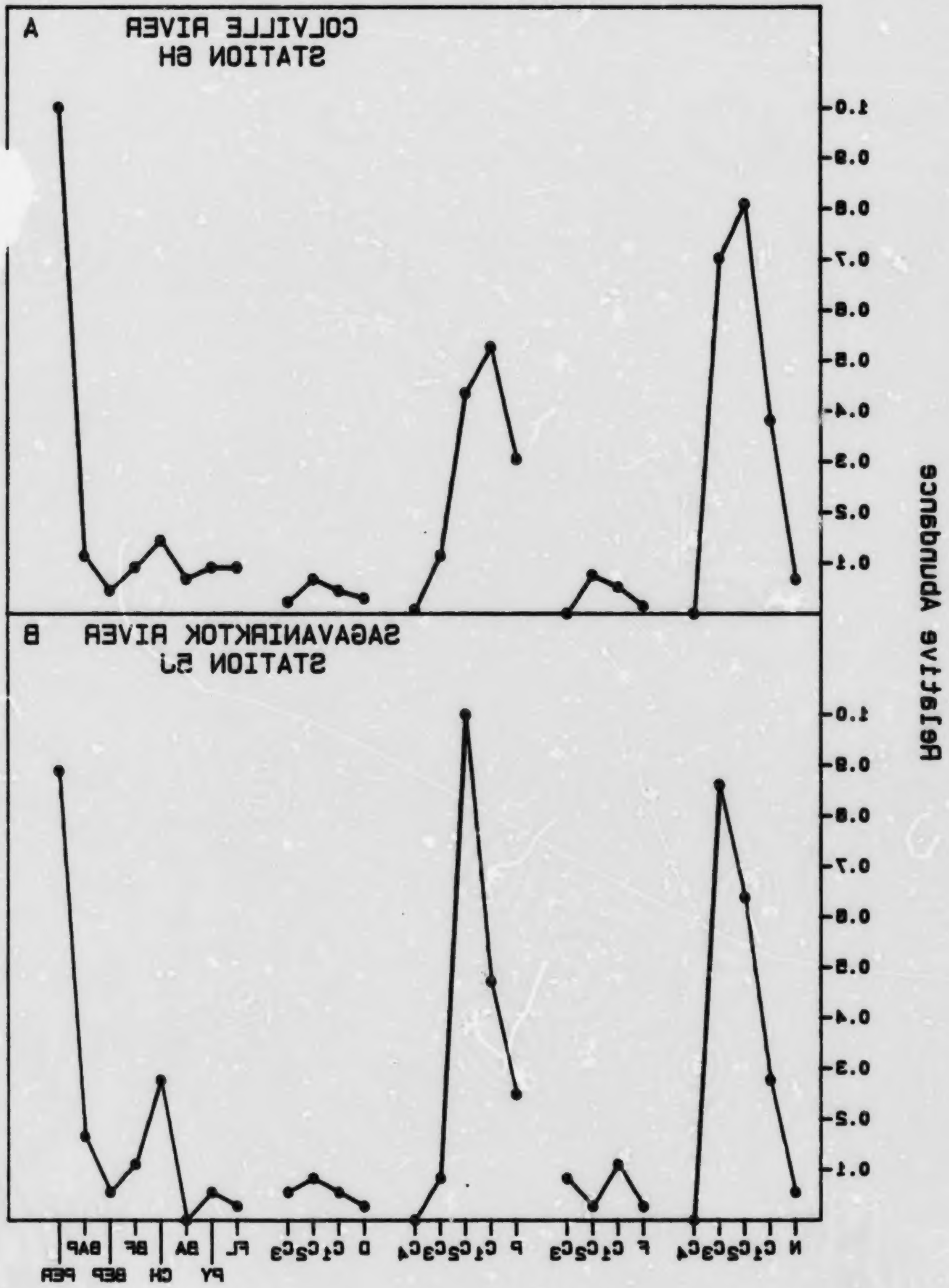

FIGURE 7.25 RELATIVE BUNDANCE OF AROMATIC HYDROCARBONS IN YEAR-2 RIVER SEDIMENTS

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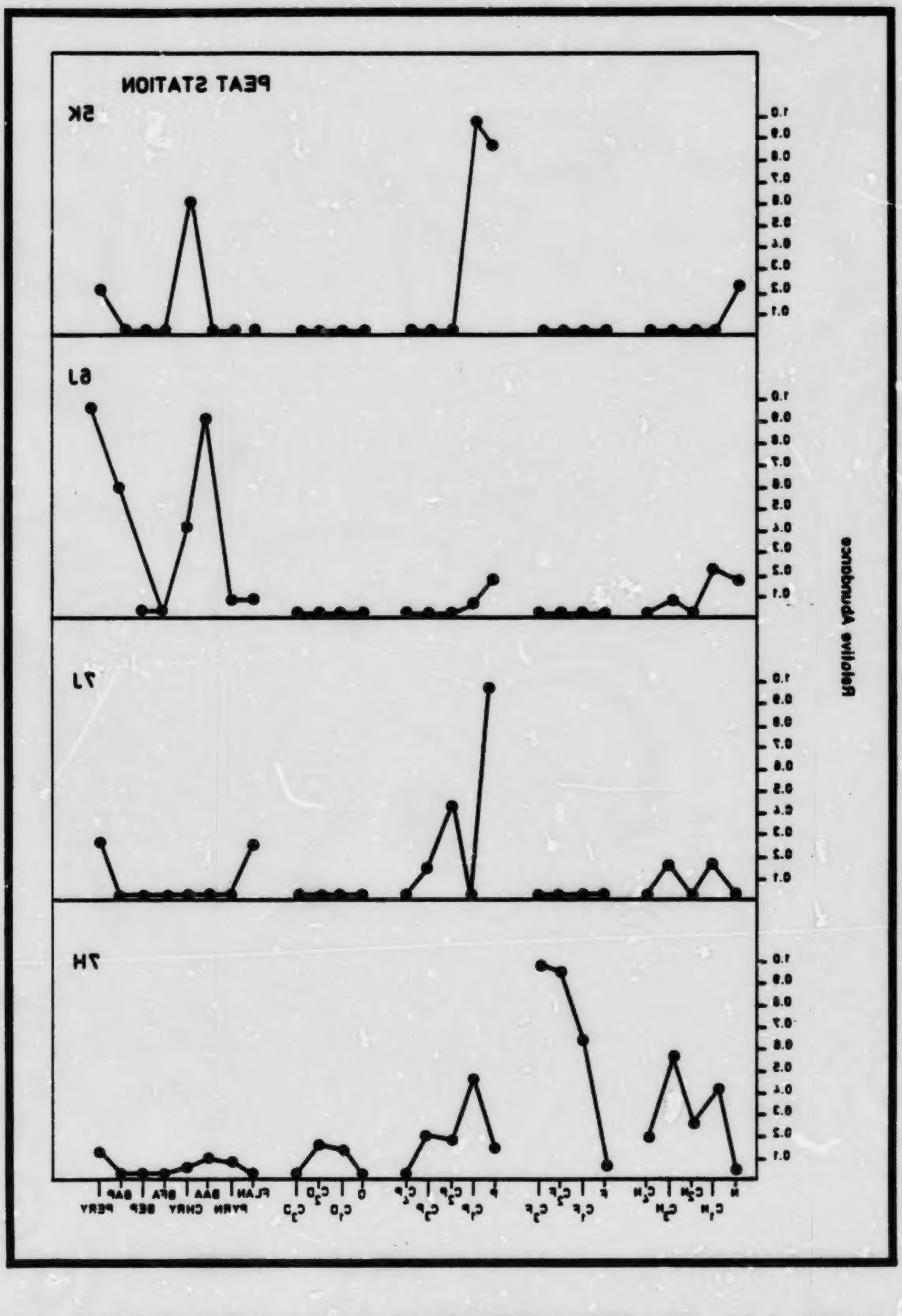

FIGURE 7.24 RELATIVE ABUNDANCE OF AROMATIC HYDROCARBONS FOR COASTAL PEAT STATIONS 5K, 6J, 7J, AND 7H

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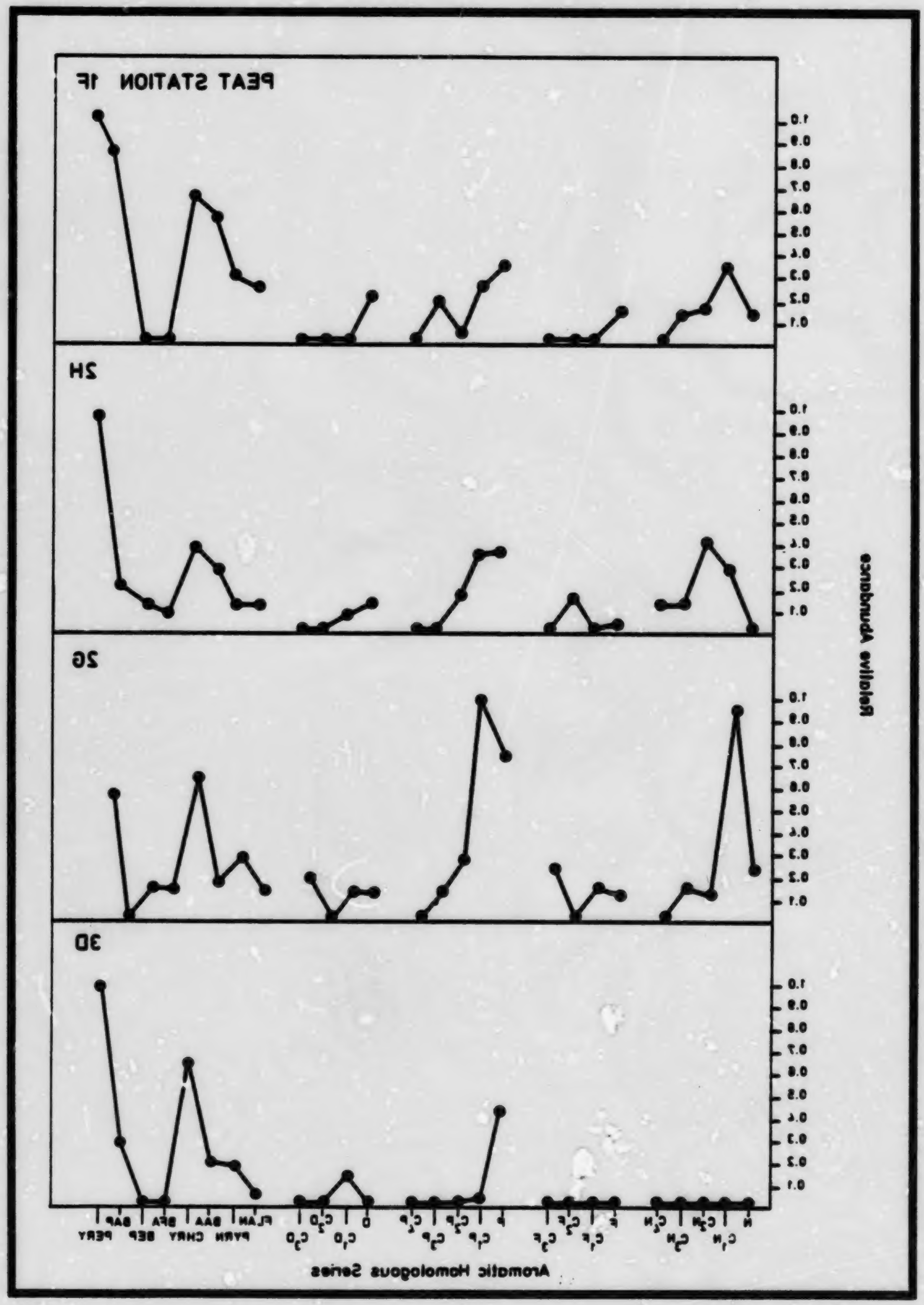

FIGURE 7.23 RELATIVE ABUNDANCE OF AROMATIC HYDROCARBONS FOR COASTAL PEAT STATIONS 1F, 2H, 2G, AND 3D

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TABLE 7.23 KEY AROMATIC HYDROCARBON PARAMETERS AND RATIOS IN COASTAL PEAT AND RIVER SAMPLES.

Peat Stations	ΣPAH[a]	FFPI	N/P	P/D	PAH/TOC[b]
1F	0.62	0.34	0.91	3.9	10
2G	0.17	0.70	0.09	5.0	4
2H	0.41	0.48	1.1	4.3	2.4
3D	0.18	0.10	-	1.1	0.8
5K	0.05	0.72	0.12	-	0.6
6J	0.20	0.19	1.8	-	0.8
7H	0.71	0.95	1.4	4.0	30
7J	0.05	0.78	0.20	-	0.16
Average Peat	0.30	0.53	1.1	3.7	-
River Stations					
2J	0.19	0.89	0.98	7.1	4.6
5J	0.21	0.72	1.0	8.1	20
5L	0.46	0.80	1.3	2.5	2.5
5M	0.05	0.49	0.68	3.8	1.2
6K	0.66	0.71	1.4	4.2	7.1
6H	0.70	0.70	1.4	8.3	10
Average River	0.38	0.72	1.1	5.7	7.6
3-Year Average Marine Sediments	0.44	0.77	1.2	5.6	13

[a] µg/g dry weight

[b] x 10^3

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compounds and with the general lack of high molecular weight olefins. The result is that the LALK/TALK ratio in the river sediment is quite similar to that found in coastal offshore sediment. Coastal peat along the river banks is certainly an important source of hydrocarbons to the river sediments. However, it is this distribution of LALK compounds that differentiated river sediment from coastal peat and suggested that an upriver source of fossil hydrocarbons (coal and/or oil) combined with peat to form the composition in the river sediments. In turn, it appears that the river and offshore sediments were quite similar in composition.

The PAH distributions of peat and river sediments were also instructive. The aromatic content of peat and river sediments was high and it was clear that a combination of these sources contributed to the high PAH content of the offshore sediment. The total PAH content (2 to 5 rings) of peat averaged 0.30 µg/g and ranged from 0.05 to 0.71 µg/g, while the offshore sediments averaged 0.44 µg/g. On the basis of PAH concentration comparisons, it is possible that the PAH in offshore sediments originated in a combination of peat and river sediments. Key PAH ratios shed more light on the issue. The tabulated average ratios in Table 7.23 indicate the following:

- The N/P ratios of peat, river, and offshore sediments are, on the average, similar.

- The P/D ratios of river and offshore sediments are similar and differ from peat.

- The mean PAH/TOC ratios in the offshore sediments are similar to the river samples and quite different from the peat samples.

- The FFPI is similar in river and offshore sediments, both of which are higher than peat. A similarity in offshore and river sediment is apparent and appears to stem from similarities of the N and P series of aromatics. The lower value of the FFPI in peat indicates that river sediments are the major source of the N and P series. The source of fossil N and P appears to be coincident with the LALK distribution observed for the saturated hydrocarbons.

To further examine the PAH assemblages, alkyl homologue distributions of the peat and river sediment are plotted in Figures 7.23 through 7.26. When viewed in comparison to the

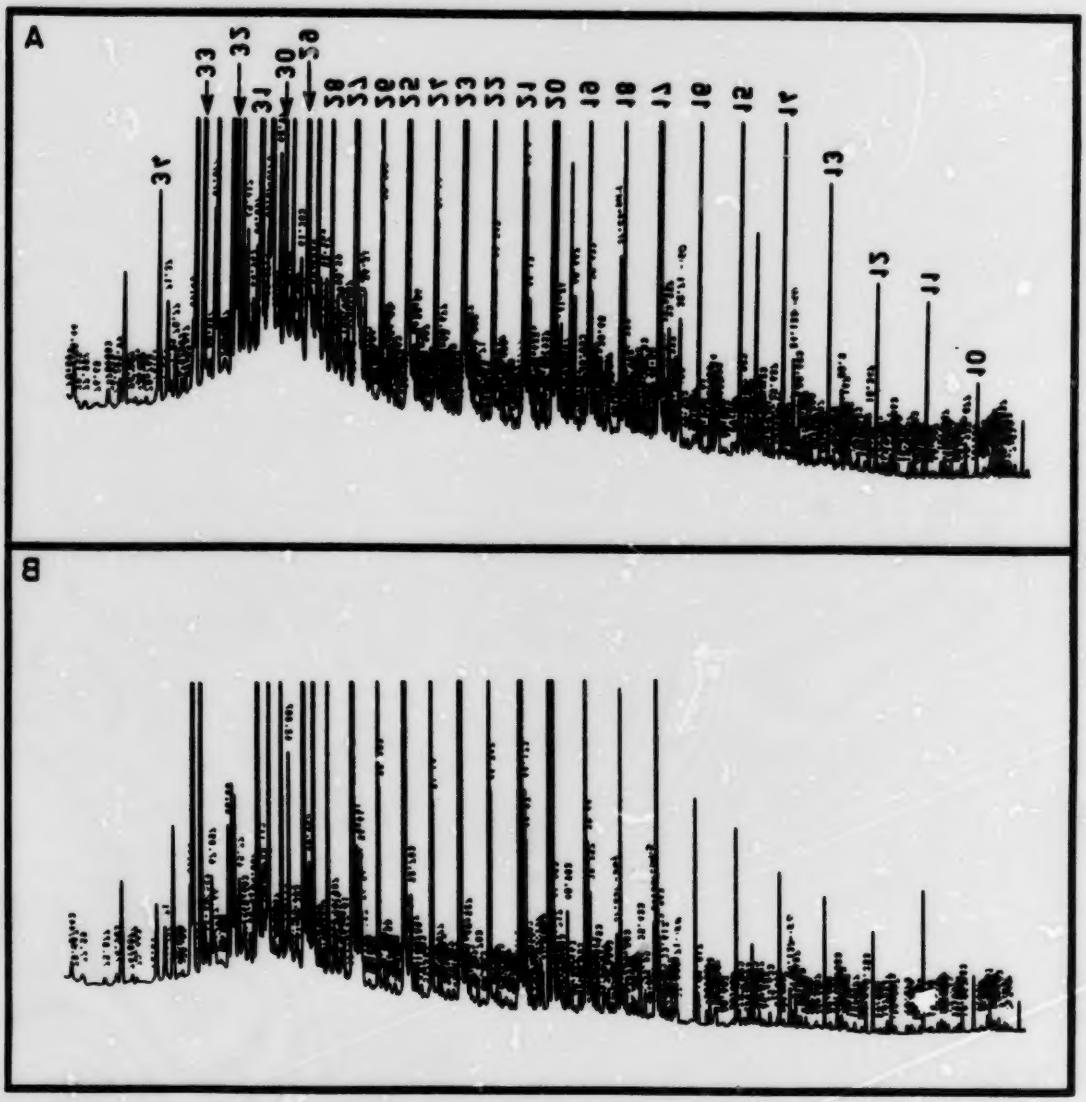

FIGURE 7.22 FLAME IONIZATION DETECTION GAS CHROMATOGRAMS SHOWING SATURATED HYDROCARBON COMPOSITIONS OF COLVILLE RIVER (A) AND SAGAVANIRKTOK RIVER (B) SEDIMENTS

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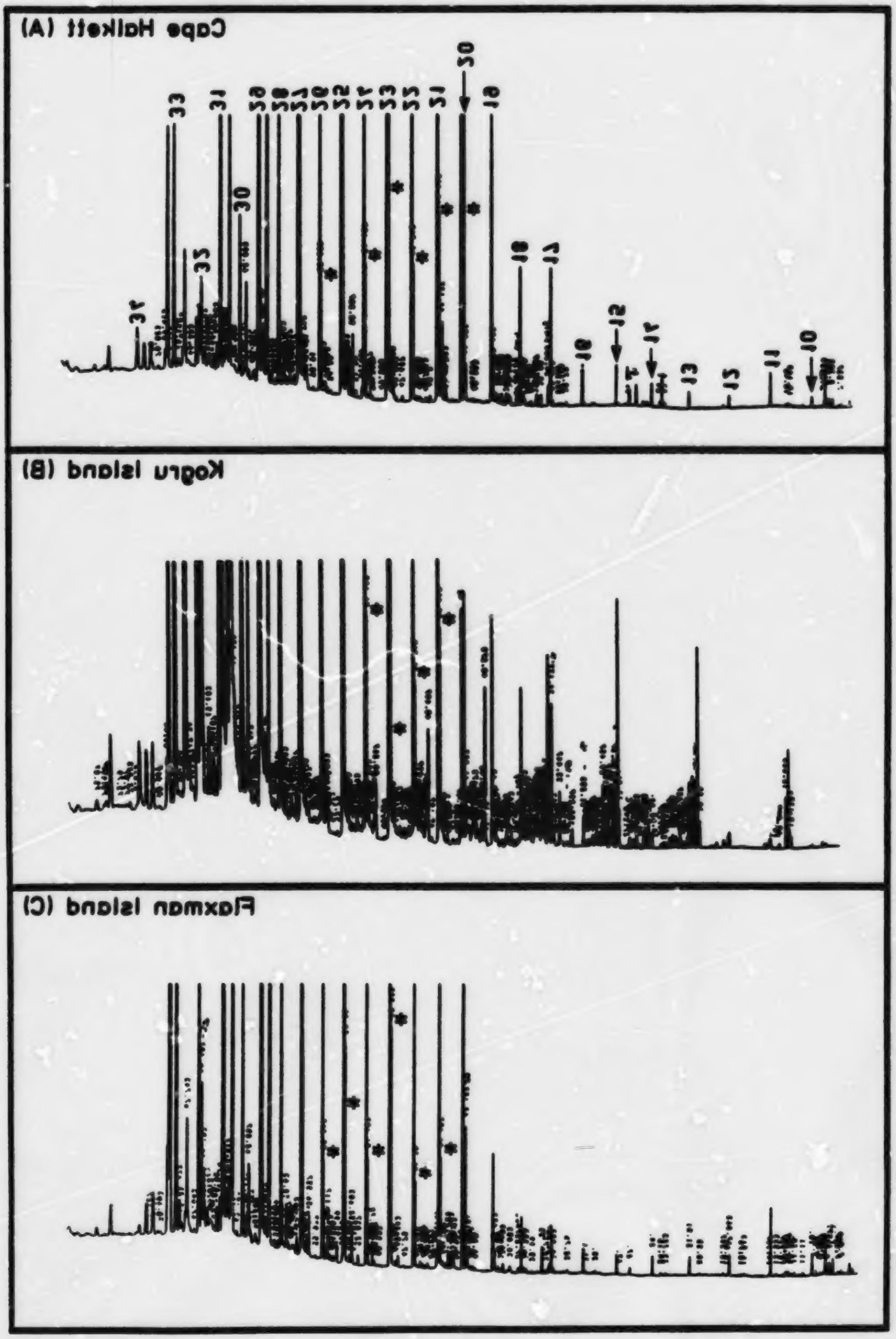

FIGURE 7.21 FLAME IONIZATION DETECTION GAS CHROMATOGRAMS SHOWING SATURATED HYDROCARBON COMPOSITIONS OF COASTAL PEAT (ASTERISK INDICATES MONO-OLEFIN)

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TABLE 7.22 KEY SATURATED HYDROCARBON PARAMETERS AND RATIOS IN COASTAL PEAT AND RIVER SAMPLES

	LALK[a]	TALK[a]	LALK/TALK	PRIS[a]	PHY[a]	PRIS/PHYT	ISO/ALK	TOT[a]	TOC[b]	TOT/TOC
Peat Stations										
1F	12	260	0.044	0.015	<D.L.[c]	–	0.02	232	9.5	0.029
2G	0.86	39	0.021	0.021	0.008	2.6	0.20	50	4.2	0.056
2M	2.8	84	0.033	0.066	0.043	1.5	0.12	110	17	0.012
3D	3.7	230	0.015	0.071	0.040	1.3	0.15	390	23	0.007
5K	1.3	83	0.016	0.034	0.022	1.5	0.25	150	9.3	0.017
6J	5.9	240	0.024	0.026	<D.L.	–	0.03	740	26	0.017
7H	1.7	41	0.042	0.042	0.023	1.8	0.19	51	2.3	0.022
7J	17	600	0.028	2.65	0.075	35	0.43	1700	30	0.058
Average Peat			0.028 ± 0.01				0.17 ± 0.13			0.027 ± 0.02
River Stations										
2J	0.4	1.2	0.34	0.031	0.014	2.2	0.38	3	41	0.062
5L	1.3	14	0.10	0.051	0.036	1.4	0.23	32	185	0.176
5J	1.1	8.7	0.13	0.025	0.020	1.3	0.21	16	1.3	0.012
5M	0.73	4.1	0.21	0.009	0.005	0.7	0.20	9	42	0.195
6H	1.2	11	0.12	0.02	0.038	2.5	0.45	25	6.6	0.004
6K	0.87	8.3	0.11	0.09	0.042	2.2	0.57	18	93	0.225
Average River			0.17 ± 0.09			1.7	0.34 ± 0.14			0.112 ± 0.098
3-Year Average Marine Sediments			0.17			2.1	0.45			0.015

[a] µg/g Dry weight
[b] mg/g Dry weight
[c] Detection limit

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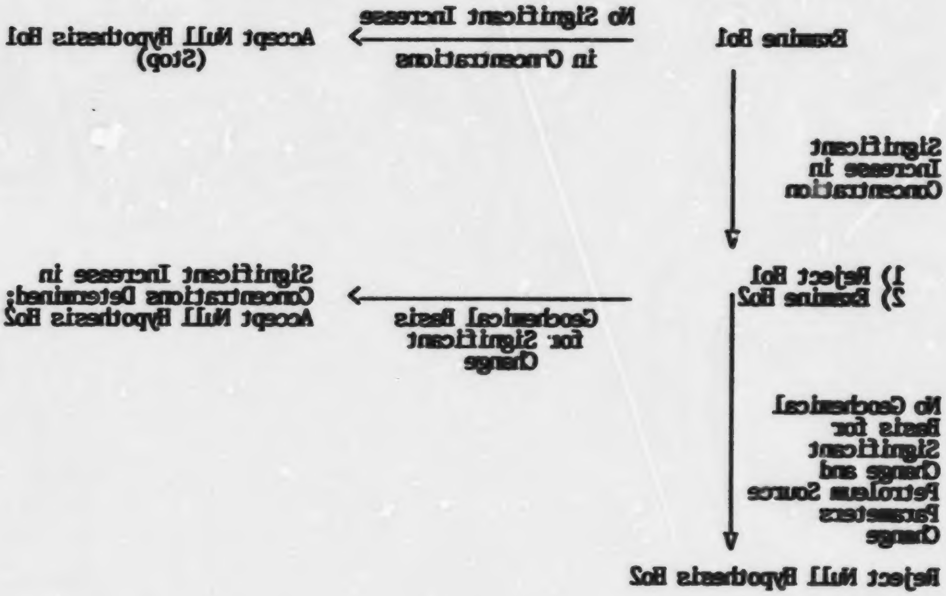

FIGURE 8.1 SCHEMATIC FOR HYPOTHESIS TESTING

which the true average concentration can be found 95 percent of the time. The results of this technique are presented in Section 8.5.

- **Analysis of Variance (ANOVA)** -- This analysis was used to determine year-to-year differences (effects) in the concentrations of selected parameters and to make station-to-station comparisons of the same parameter concentrations. An advantage of employing ANOVA methods is that both effects can be modeled and assessed in the same analysis. The results for the ANOVA methods used in this study are presented in Sections 8.6 through 8.9.

One result of any statistical test is a probability value (p-value). A p-value is the probability of obtaining the observed (or more extreme) data if, in fact, the null hypothesis is true. Small p-values indicate that the data are inconsistent with the null hypothesis. Specific null hypotheses that are tested in this investigation are

Ho1: There will be no change in sediment concentrations of selected metals or hydrocarbons.

Ho2: Changes in concentrations of selected metals or hydrocarbons in sediments are not related to oil and gas development activity.

Ho3: There will be no change in the concentrations of selected metals or hydrocarbons in selected sentinel organisms.

Ho4: Changes in concentrations of selected metals or hydrocarbons in selected sentinel organisms are not related to OCS oil and gas development activity.

These same hypotheses would also be examined in any future investigation.

An approach that can be used to test the null hypotheses Ho1 and Ho2 is outlined in Figure 8.1. Ho1 will be accepted if the incremental (e.g., Year-1 to Year-3) change in the mean metal or hydrocarbon concentrations between years is not significant according to the selected variance test. If it is found that the change in the mean concentration is significant (i.e., Ho1 is rejected), according to the criteria of the test, hypothesis Ho2 will be examined. Ho2 considers the source ratios which have been or will be selected to indicate the influence of oil and gas development activity on the observed metal or hydrocarbon concentrations. If Ho2 testing indicates

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Data from all three years of the monitoring effort are used to characterize certain geographic regions of the Beaufort Sea Study Area, as well as each individual station. This characterization consists of descriptive statistics and appropriate graphics to summarize information on the concentrations of the selected analytes found in both the marine sediments and tissue samples. Some statistical tests are performed and variability estimates calculated to aid in the interpretation of analyte concentration patterns among stations. Because there was little oil drilling activity in the Study Area during the three years of the study, these results could be viewed as "baseline" information for future monitoring efforts. The interpretation of the data in Section 7.0 indicates that this is indeed the case.

The present study also requires the definition of specific statistical models and methods to be used for future investigations. For example, it will be of interest to compare the sediment concentrations of barium, at some future date, to the baseline concentrations after more extensive oil exploration and development operations have begun. It will also be of interest to compare future concentrations of analytes with baseline concentrations for each station. To illustrate the statistical methods that can be useful in future monitoring investigations, data from a selected group of four stations in the vicinity of the Endicott Field development were chosen for testing. In addition, these methods were employed in the analysis of concentration gradients seaward from the Colville River. Results of these statistical analyses will allow researchers to make inferences about the effects of oil and gas exploration and development activities in the Beaufort Sea.

8.2 STATISTICAL METHODS

Several statistical analysis methods were used to examine trends or patterns in the sediment and tissue data as well as to assess the probability of making correct inferences from these examinations. The statistical methods applied to the data chosen included:

- **Principal Component Analysis (PCA)** -- As a pattern recognition tool, PCA was used to explore similarities among stations by considering each station a multivariate observation (i.e., multiple parameters were measured at each station). This method and the results are described in Section 8.4.
- **Confidence Interval Estimation** -- This method was used to estimate the upper and lower bounds of the parameter concentrations measured. This descriptive technique provides the interval within

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8.0 STATISTICAL ANALYSES AND DATA INTERPRETATION

8.1 INTRODUCTION

Three important findings emerge from the data analyses performed in this investigation. Each is the result of an exhaustive effort to describe and summarize the data. We have attempted to address the important issues of the three-year monitoring program in ways that lend themselves to formal statistical inferences, where these apply.

The three major findings in the statistical analysis are as follows:

- The results of the data analysis show that there is year-to-year variability in analyte concentrations and that there is insufficient evidence to conclude that these changes are due to oil and gas activities. These data can, therefore, be considered to represent the "present status" of the Beaufort Sea sediments and tissues.
- The study area within the nearshore Beaufort Sea can be viewed as a collection of geographic regions. Some regions are shown to be statistically very similar; others are distinctly different.
- Rivers emptying into the Beaufort Sea appear to be important sources of selected chemical components to the marine sediments.

Evidence to support the above conclusions is presented in Sections 8.4 through 8.10 below. Appendix C contains the detailed results of the statistical analyses for the Beaufort Sea Monitoring Program (BSMP). Most of the figures and tables completed in the statistical analyses are placed in this appendix for the convenience of the reader.

There are two objectives for the statistical analyses performed in this study:

- To characterize the concentrations of selected analytes in the marine sediments and sentinel organisms, and to characterize the variability of these concentrations.
- To develop statistical methods for testing hypotheses concerning the impact of oil and gas exploration and development activity.

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TABLE 7.26 MODE OF FEEDING FOR ANIMAL SPECIES COLLECTED AND ANALYZED

Genus	Mode of Feeding
Anonyx	Migratory Surface Scavenger
Astarte	Filter Feeder
Cyrtodaria	Filter Feeder
Macoma	Deposit Feeder
Portlandia	Deposit Feeder

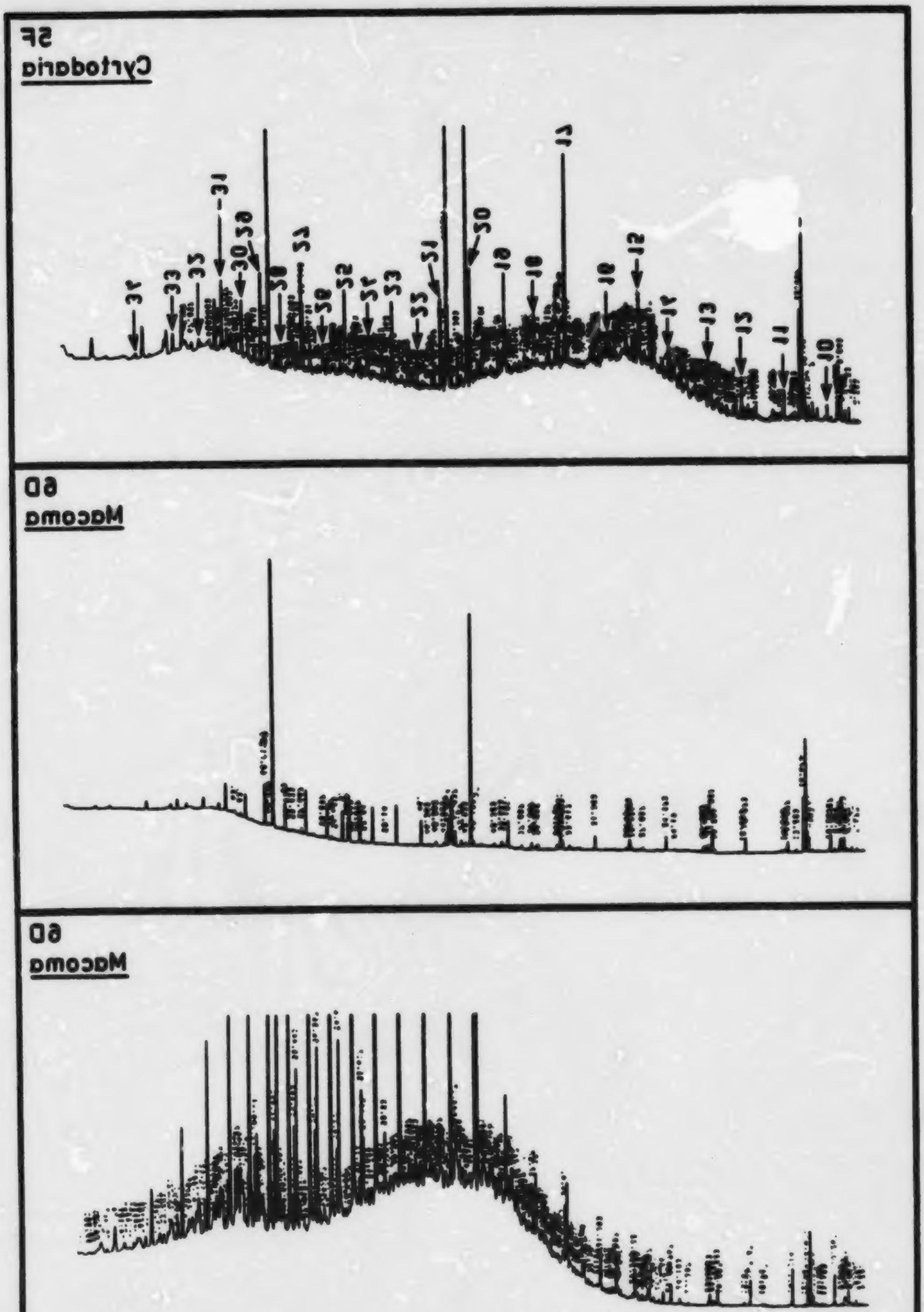

FIGURE 7.33 FLAME IONIZATION DETECTION GAS CHROMATOGRAMS SHOWING SATURATED HYDROCARBON COMPOSITION OF *CYRTODARIA* AND *MACOMA*

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differed in their PAH content as well. The first replicate sample shown in Figure 7.33 (center) contained 0.006 μg/g of naphthalenes and no phenanthrenes or dibenzothiophenes; the second replicate (Figure 7.33 bottom) contained 0.07 μg/g of naphthalenes, 0.004 μg/g phenanthrenes, and 0.002 μg/g of dibenzothiophenes. These potential differences among replicates must be taken into account when interpreting monitoring data.

The GC traces of *Cyrtodaria* from all four replicates at Station 5F (Figure 7.33 top) and Station 6G indicated the presence of a bimodal UCM and n-alkane feature. This, together with the detectable, but very small, quantities of PAH, indicated little evidence for petroleum inputs. Ironically, the species with highest PAH contents (Table 7.25) were least likely to indicate petrogenic input from the saturated hydrocarbon GC traces.

Hydrocarbons in solution or dispersion in seawater are much more bioavailable than hydrocarbons sorbed to sediments or detritus (Neff, 1979; Neff and Anderson, 1981; Anderson, 1983). The bioaccumulation factor (concentration in tissues divided by concentration in sediment) for aromatic hydrocarbons associated with sediments and detritus usually is less than 1, but may be as high as 11. Bioavailability is inversely related to sediment organic carbon content. However, because sediments represent, by far, the most concentrated source of hydrocarbons in the contaminated environment, sediments are a major source of chronic contamination of benthic fauna in an oil-impacted area. It appears that filter-feeding bivalves accumulate petroleum hydrocarbons primarily from the water column, but deposit-feeding bivalves accumulate hydrocarbons primarily from sediments (Boehm et al., 1982a; Anderson, 1983).

Table 7.26 lists the feeding mechanisms that characterize the animals collected and analyzed in Year-2 of the BSMP. The amphipod, *Anonyx*, represents a migratory scavenger that feeds primarily on surface detritus. These animals should be considered as integrators of organic material from a region, rather than as representative of the station where collected. *Astarte* and *Cyrtodaria* are primarily suspension feeders; their tissues are expected to reflect water column (soluble low molecular weight) hydrocarbon contaminants. *Portlandia* and *Macoma* are both characterized as surficial deposit feeders. Species utilizing this mode of feeding are expected to accumulate hydrocarbons present in the sediments.

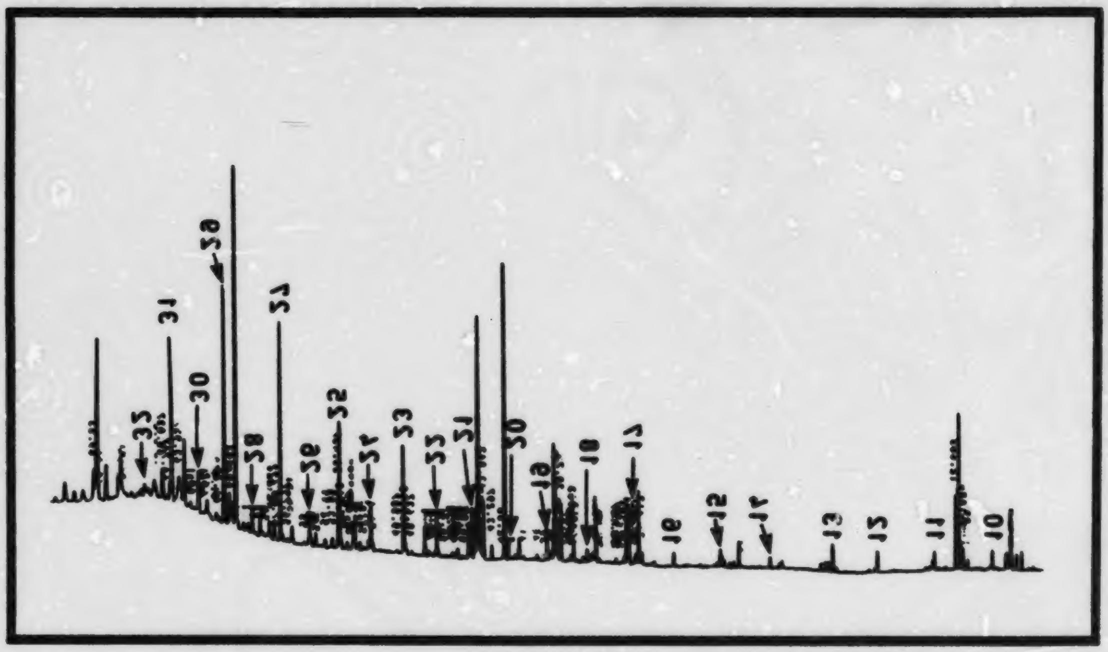

FIGURE 7.32 FLAME IONIZATION DETECTION GAS CHROMATOGRAM SHOWING SATURATED HYDROCARBON COMPOSITION OF *PORTLANDIA*

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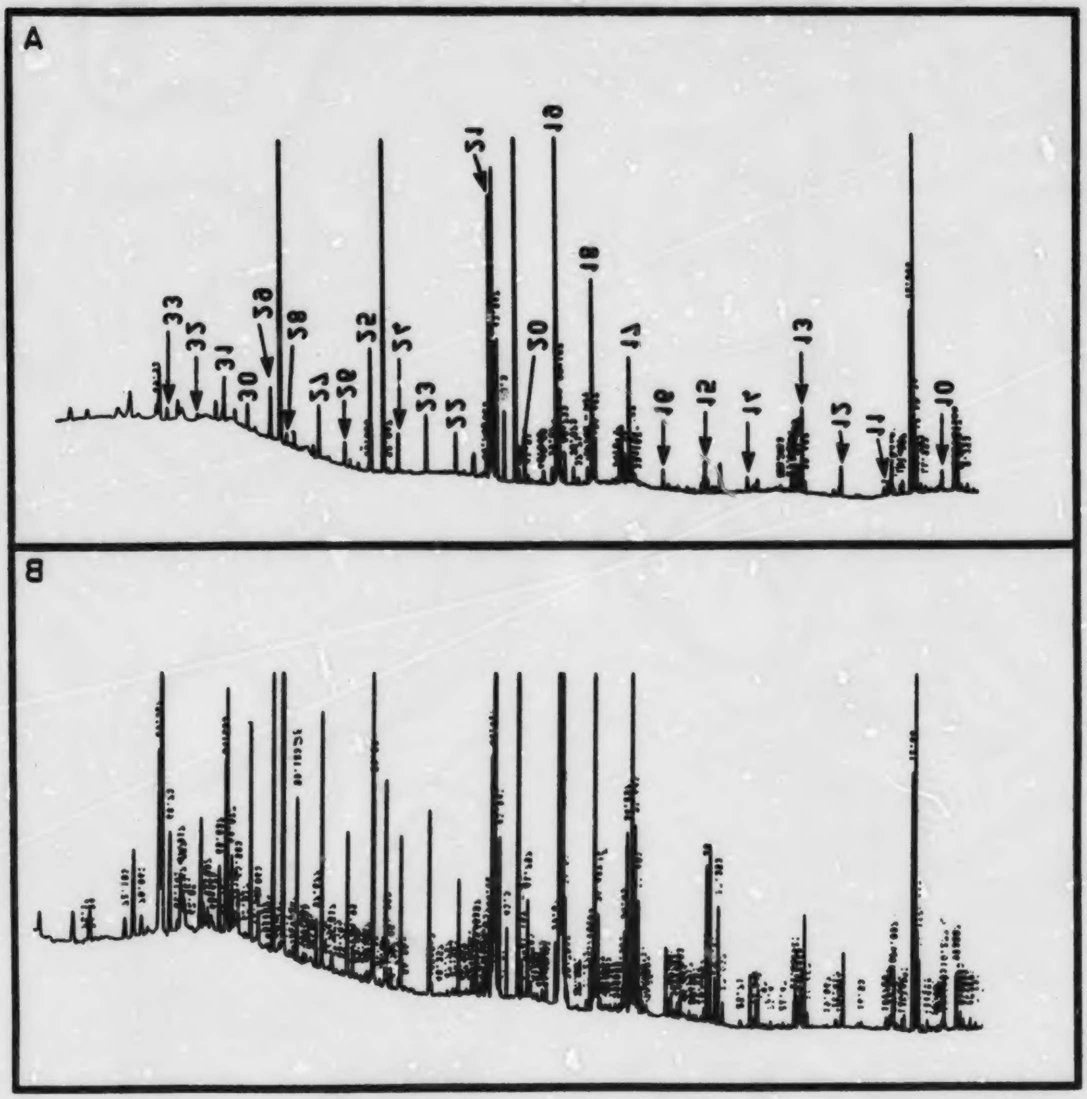

FIGURE 7.31 FLAME IONIZATION DETECTION GAS CHROMATOGRAMS SHOWING SATURATED HYDROCARBON COMPOSITION OF *ASTARTE* FROM STATIONS 6D (A) AND 3A (B)

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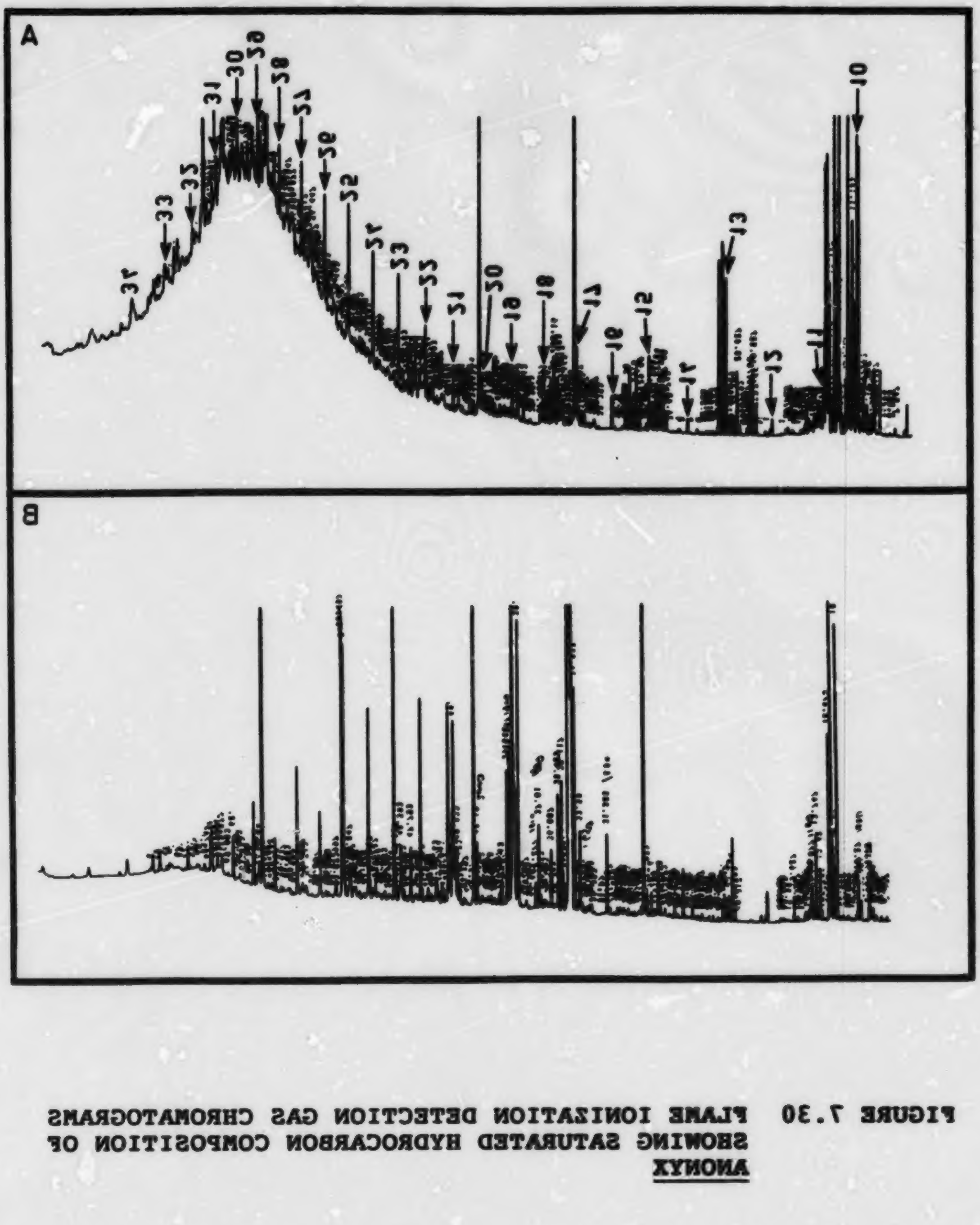

FIGURE 7.30 FLAME IONIZATION DETECTION GAS CHROMATOGRAMS SHOWING SATURATED HYDROCARBON COMPOSITION OF ANONYX

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(presumably attributable to total aromaticity). For example, all of the species contained background levels of the 3-ring aromatic series of phenanthrenes at concentrations of less than detection limit (<0.001) to 0.010 µg/g, while the 355-nm UV/F band varied from 0.75 to 8.9 µg/g. The Year-2 *Portlandia* sample contained the highest UV/F and GC/MS values, *Astarte* values for both UV/F and GC/MS were intermediate, and values for *Anonyx* were lowest. Of special interest were the nondetectable to very low levels of the dibenzothiophenes (D) in the animals. These compounds are very important components of Prudhoe Bay crude oil and presumably other north slope crudes. The absence of dibenzothiophene compounds in tissues underlines the usefulness of this parameter and the P/D ratio in future monitoring of oil and gas inputs to the environment. In fact, the very low levels of all aromatic hydrocarbons in the tissues indicate that tissue PAH levels may be very powerful monitoring parameters.

The low levels of aromatic hydrocarbons in the tissues, first revealed in Year-1, were remarkable in view of the large sediment reservoir of PAH compounds that were apparently not bioavailable. There was no relationship between PAH in tissues and sediments of the Beaufort Sea in the range of animal species examined.

The saturated hydrocarbon characteristics of the various species examined, as indicated by the GC traces, are presented in Figures 7.30 through 7.32. Two examples of GC traces from the amphipod *Anonyx* are shown in Figure 7.30. The chromatogram from Figure 7.30 (A) exhibited an abundance of higher molecular weight n-alkanes (see Table 7.25) and a unimodal unresolved complex mixture (UCM) or "hump". These features can be mistakenly attributed to petroleum inputs. However, the lack of a significant PAH content precluded the assignment of the components observed in Figure 7.30 to petroleum. The UCM may be of microbial, rather than petroleum, origin. Not all of the *Anonyx* samples were similar in composition. The sample from Station 7E (Figure 7.30 B) contained the n-alkanes, but little of the UCM distribution. The bivalve *Astarte* (Figure 7.31) contained saturated hydrocarbon distributions that are similar at all stations (3A, 6D, 1A, and 5H). The distribution shown in Figure 7.31 (A) and expanded in Figure 7.31 (B) was observed at all stations. Prominent were n-alkanes and "clusters" of mono-olefinic hydrocarbons surrounding the n-C13 through n-C21 alkanes.

Portlandia from Station 1A (Figure 7.32) contained a GC distribution indicative of biogenic inputs and sediment hydrocarbon material was apparent (n-C25, n-C27, n-C31). The two replicates of *Macoma* from Station 6D (Figure 7.33) contained markedly different distributions; one indicated very small quantities of hydrocarbons and the other obviously contained sediment-associated hydrocarbons, as evidenced by the high molecular-weight alkanes and UCM. The two *Macoma* replicates

TABLE 7.25 AVERAGE CONCENTRATIONS OF SELECTED AROMATIC AND SATURATED HYDROCARBON PARAMETERS IN ANIMAL TISSUES

		N^a	P^a	D^a	P/D	PHE^a	$TALK^a$	$LALK^a$
Anonyx								
5H	Year-3	<D.L[b]	<D.L	<D.L	—	<D.L	0.9	0.33
1A/B/E	Year-2	0.029	<D.L	<D.L	—	<D.L	10.9	0.30
	Year-3	0.008	<D.L.	<D.L	—	<D.L	2.3	0.26
4B	Year-2	0.015	<D.L.	<D.L	—	0.001	10.6	0.20
	Year-3	—	—	—	—	—	—	—
6G	Year-2	0.009	<D.L	<D.L	—	<D.L	14.5	0.94
	Year-3	—	—	—	—	—	—	—
7B/C	Year-2	0.004	<D.L	<D.L	—	<D.L	27.3	0.87
	Year-3	0.006	<D.L	<D.L	—	<D.L	0.8	0.09
7E	Year-2	0.008	0.001	<D.L	—	<D.L	6.0	3.8
	Year-3	0.013	<D.L	<D.L	—	<D.L	0.9	0.19
Astarte								
5(1)	Year-3	0.011	<D.L	<D.L	—	<D.L	1.2	0.10
1A+1B	Year-2	0.014	0.005	0.002	2.5	0.007	5.0	2.7
	Year-3	0.008	<D.L	<D.L	—	<D.L	.18	0.18
3A	Year-2	0.003	0.003	<D.L	—	0.001	3.6	0.60
	Year-3	0.002	<D.L	<D.L	—	0.007	1.5	0.04
5H	Year-2	0.002	0.002	<D.L	—	0.002	2.3	0.30
	Year-3	0.004	<D.L	<D.L	—	0.001	5.0	0.11
6D	Year-2	0.007	0.004	0.002	2.0	0.008	1.2	0.46
	Year-3	0.014	0.001	<D.L	—	0.001	0.80	0.10
2F	Year-3	0.007	<D.L	<D.L	—	<D.L	1.6	0.20
Cyrtodaria								
5F	Year-1	<D.L	<D.L	<D.L	—	<D.L	0.8	0.35
	Year-2	0.003	0.002	<D.L	—	0.002	3.7	0.29
	Year-3	0.018	0.011	0.003	3.5	0.005	0.7	0.10
6G	Year-2	0.004	0.005	<D.L	<D.L	0.005	3.6	0.51
	Year-3	0.003	0.003	<D.L	—	0.005	0.4	0.04
Portlandia								
1A	Year-2	0.009	0.009	<D.L	—	0.016	7.0	0.43
	Year-3	0.013	0.004	<D.L	--	0.002	3.1	0.20
Macoma								
6B	Year-2	0.035	0.002	0.001	2.0	0.008	13.0	0.14

[a] Wet Weight in ug/g

[b] Detection Limit

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TABLE 7.24 RESULTS OF UV/F ANALYSIS OF YEAR-3 TISSUE SAMPLES (GIVEN IN UNITS OF PRUDHOE BAY OIL EQUIVALENTS).

Station	Species	312nm	355nm	425nm
1A	Anonyx	ND	2.59	2.59
		ND	2.05	2.46
		ND	2.36	3.02
	Portlandia	19	7.72	1.26
		17	6.55	MDL
		22	6.09	MDL
	Astarta	ND	3.47	1.80
1B	Anonyx	ND	1.00	3.16
		ND	1.08	5.64
		ND	0.52	1.51
	Astarte	ND	3.02	1.34
		ND	2.65	1.43
		ND	3.22	1.60
2F	Anonyx	38	MDL	MDL
		45	MDL	MDL
		30	MDL	MDL
3A	Astarte	12	2.47	MDL
		17	2.44	MDL
		11	1.67	MDL
5(1)	Astarte	30	3.37	MDL
5F	Cyrtodaria	27	2.36	1.75
		ND	2.07	1.76
		29	1.83	1.77
5H	Astarte	17	2.57	MDL
		17	2.16	MDL
		15	2.24	MDL
	Anonyx	22	1.57	MDL
6D	Astarte	ND	1.46	1.80
		38	3.54	3.51
		41	2.63	MDL
6G	Cyrtodaria	16	1.56	MDL
		21	1.79	MDL
		16	2.64	1.68
7B	Anonyx	11	2.80	0.79
		12	2.94	MDL
		7	0.96	1.03
7C	Anonyx	ND	2.33	1.34
		ND	10.80	2.59
		ND	1.94	1.29
7E	Anonyx	8	1.03	MDL
		ND	1.03	MDL
		12	1.27	MDL

MDL = Method Detection Level
ND = No Data

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(Figure 7.28) samples exhibited a large maximum at approximately 312 nm. This 312-nm maximum was also observed for all species examined in this study. Results for this and other studies on arctic bivalves (e.g., Boehm et al., 1982b and 1982c) indicate that the 312-nm band is a common background interference that does not correspond to any aromatic hydrocarbon content as determined by GC/MS analyses. Thus, although the intensity of the 312-nm band varies with species (Figures 7.28 and 7.29), the 355-nm band (corresponding to the 3-ring aromatics; Lloyd, 1971) appears to be most useful for diagnosing and quantifying petroleum-related inputs to the animals (Boehm et al., 1982b and 1982c). *Anonyx* and *Macoma* consistently showed low spectral intensities at 355 nm (Figure 7.28). The bivalves *Astarte*, *Portlandia*, and *Cyrtodaria* exhibited UV/F spectra with distinct spectral double bands at 355 nm and 360 nm (Figure 7.29) that resembled the sediment UV/F spectra obtained in the Year-1 program. In addition, the spectral maxima in the region greater than 400 nm indicated that higher molecular weight aromatics (e.g., perylene) were found in the animal tissues. Sediment inputs are strongly implicated.

Concentrations of Prudhoe Bay crude oil equivalents (at 355 nm) in the Year-2 tissues ranged from 0.75 to 8.8 µg/g wet weight. There appeared to be less variability within each species (*Anonyx*, 0.75 to 1.6 µg/g, representing five samples; *Astarte*, 3.3 to 4.0 µg/g, representing four samples; and *Cyrtodaria* 4.0-4.6 µg/g, representing two samples). The single sample of *Portlandia*, from Station 1A in the Camden Bay region, exhibited the highest concentration (8.9 µg/g) of Prudhoe Bay crude oil equivalents. No areal trends were revealed in these data. Thus, it can be inferred that the observed concentrations of oil equivalents represented definitive background concentrations of Prudhoe Bay crude oil equivalents. The source of this material is sediment-associated PAH.

Concentrations of Prudhoe Bay crude oil equivalents (measured at 355 nm) in the Year-3 tissues (Table 7.24) were generally similar to the Year-2 samples. In addition, as was found in Year-2, the single sample of *Portlandia* had the highest overall three-year UV/F concentration (6.8 µg/g). The three-year ranges for the other species were as follows:

Anonyx: detection limit to 5.0 µg/g
Astarte: 2.2 to 3.5 µg/g
Cyrtodaria: 2.0 to 2.1 µg/g

GC/MS analyses of the tissue samples focused on PAH content and composition. Key aromatic hydrocarbon parameters are summarized in Table 7.25. Detectable, but very low, concentrations of aromatic hydrocarbons were found in most of the samples. The GC/MS results, which yield concentrations of individual compounds, are roughly proportional to the UV/F results, which examine gross spectral characteristics

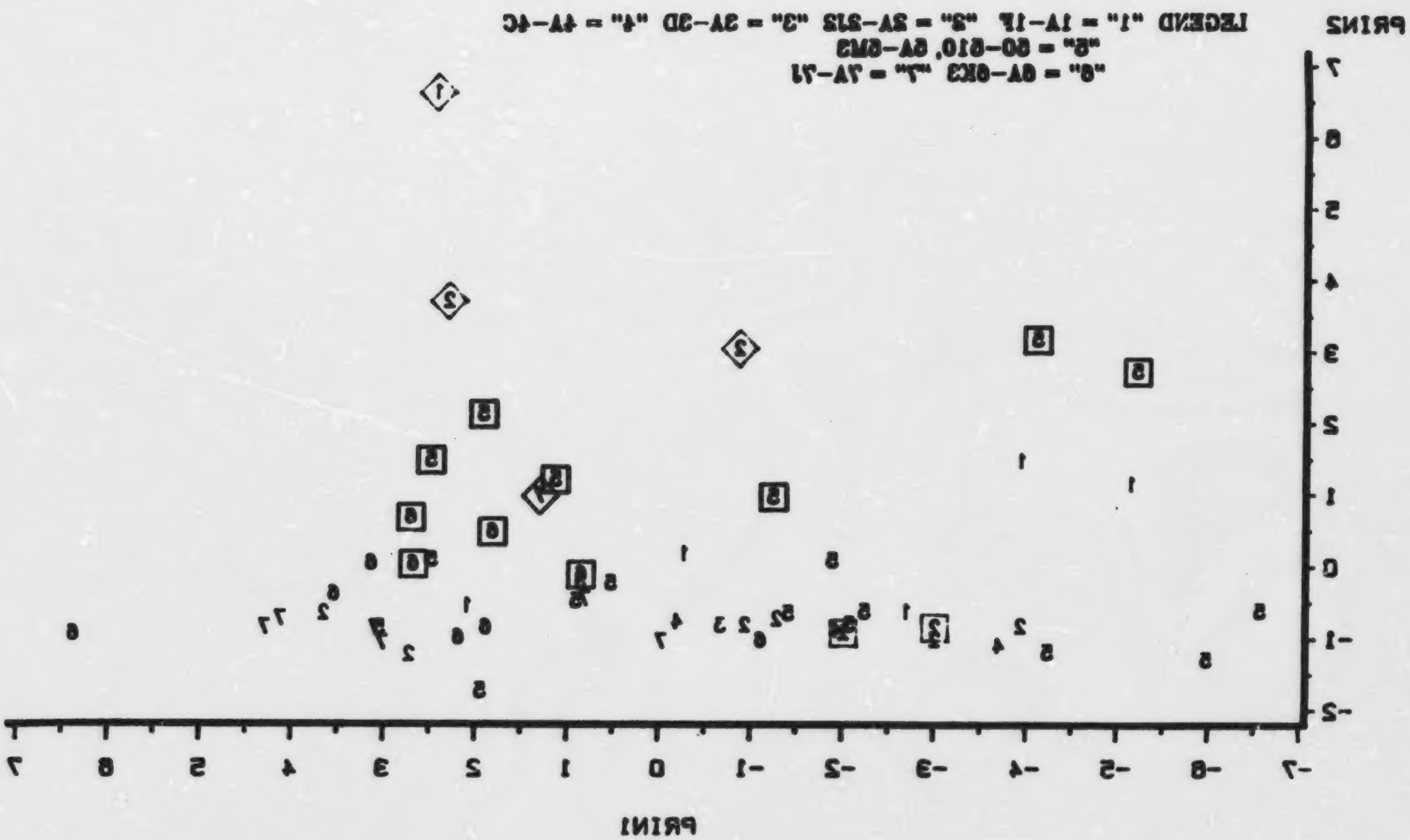

FIGURE 6.6 SCORE PLOT OF THE TWO HIGHEST PRINCIPAL COMPONENTS FOR HYDROCARBONS IN BULK SEDIMENTS FOR ALL YEARS. EACH POINT CORRESPONDS TO ONE STATION (DIAMOND-PEAT, SQUARE-RIVER).

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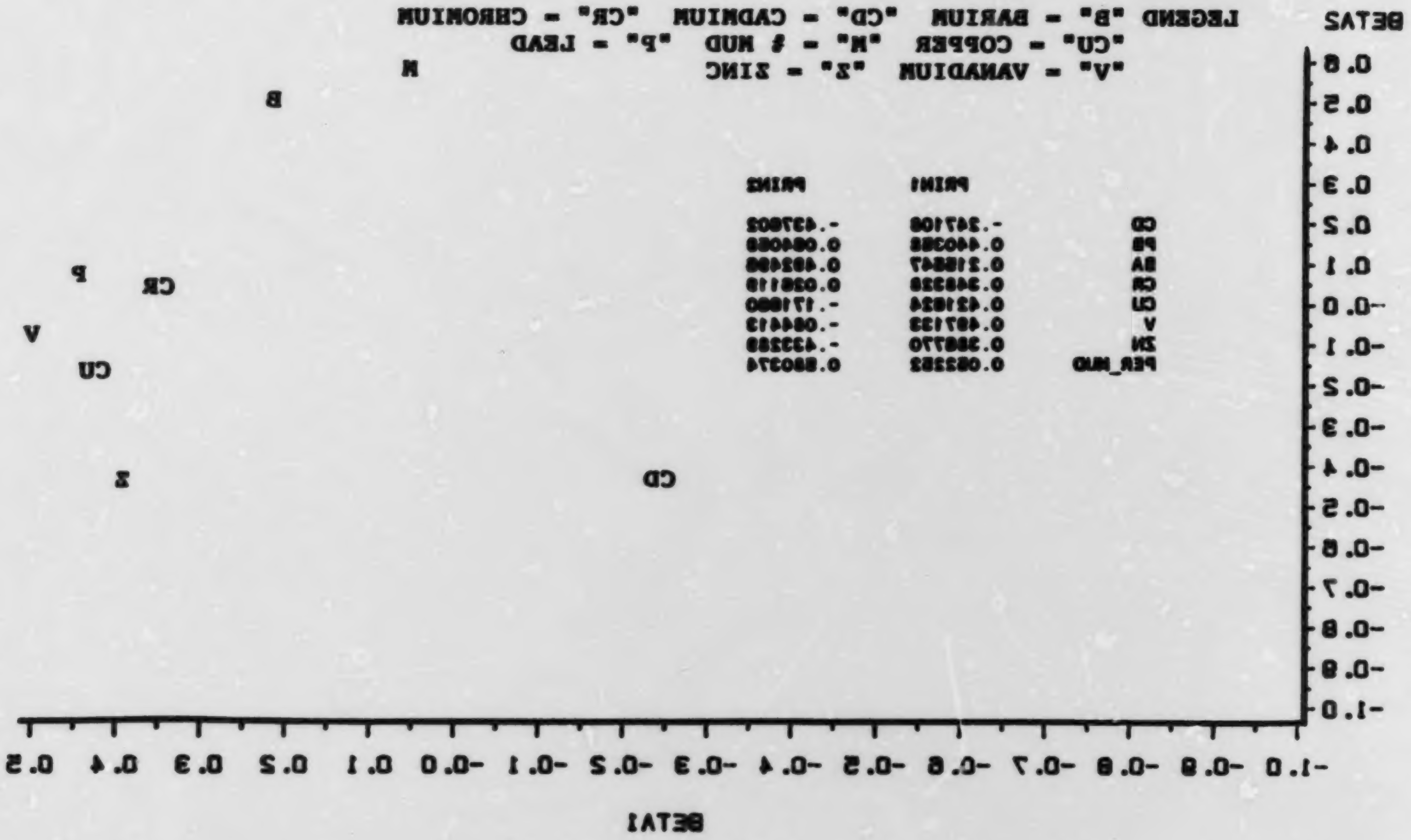

LEGEND "B" = BARIUM "CD" = CADMIUM "CR" = CHROMIUM
"CU" = COPPER "M" = % MUD "P" = LEAD
"V" = VANADIUM "Z" = ZINC

	PRIN1	PRIN2
CD	-.247108	-.437602
PB	0.440388	0.084088
BA	0.218847	0.492488
CR	0.348328	0.026119
CU	0.421824	-.171880
V	0.487133	-.084413
ZN	0.388770	-.433288
PER_MUD	0.082282	0.880374

FIGURE 8.5 LOADINGS PLOT OF THE TWO HIGHEST PRINCIPAL COMPONENTS FOR METALS IN YEAR-2 AND YEAR-3 FINE SEDIMENTS. EACH POINT CORRESPONDS TO ONE METAL.

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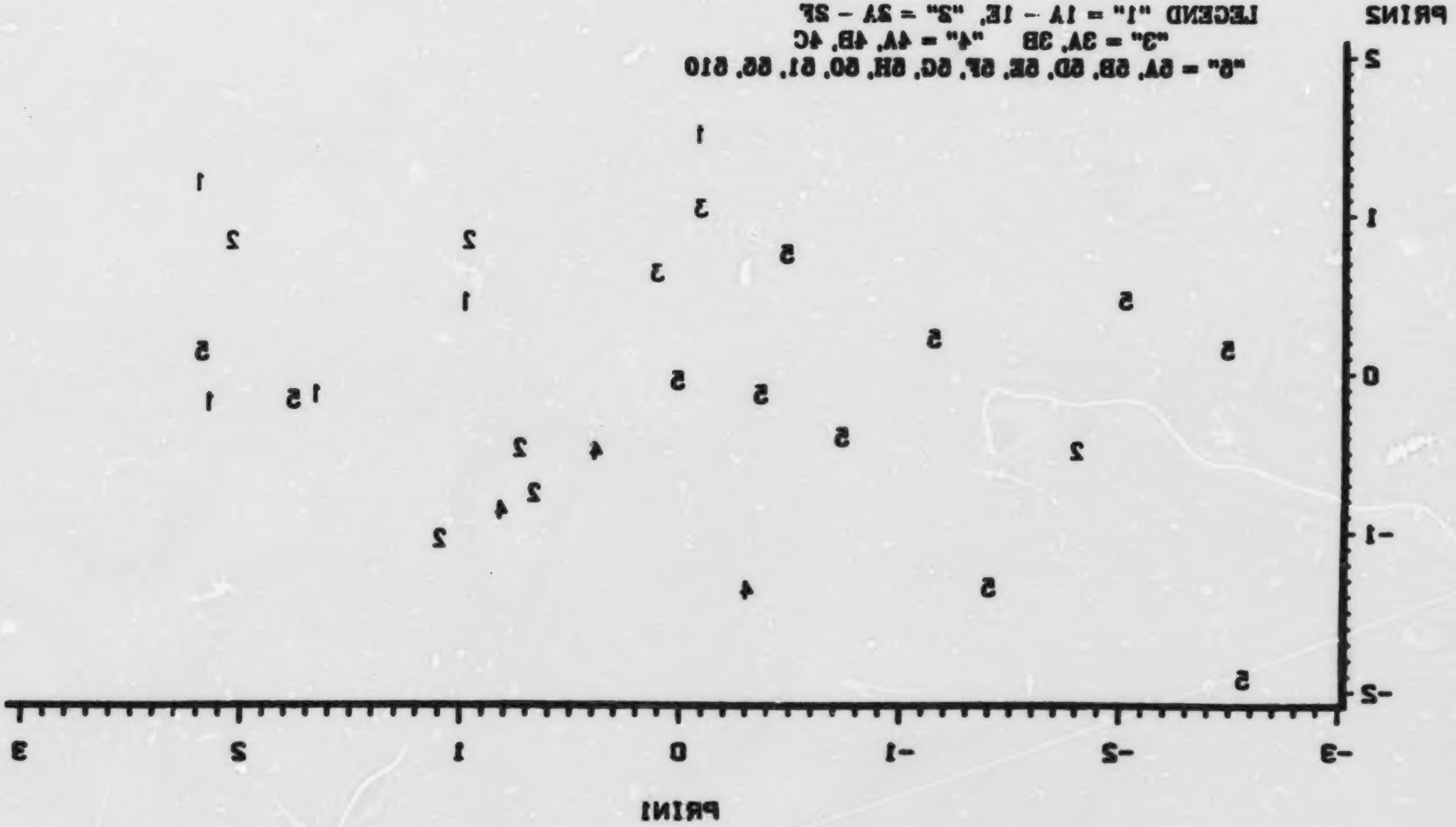

FIGURE 8.4 SCORE PLOT OF THE TWO HIGHEST PRINCIPAL COMPONENTS FOR METALS IN YEAR-2 AND YEAR-3 FINE SEDIMENTS FROM ENDICOTT FIELD AND MARINE STATIONS EAST. EACH POINT CORRESPONDS TO ONE STATION.

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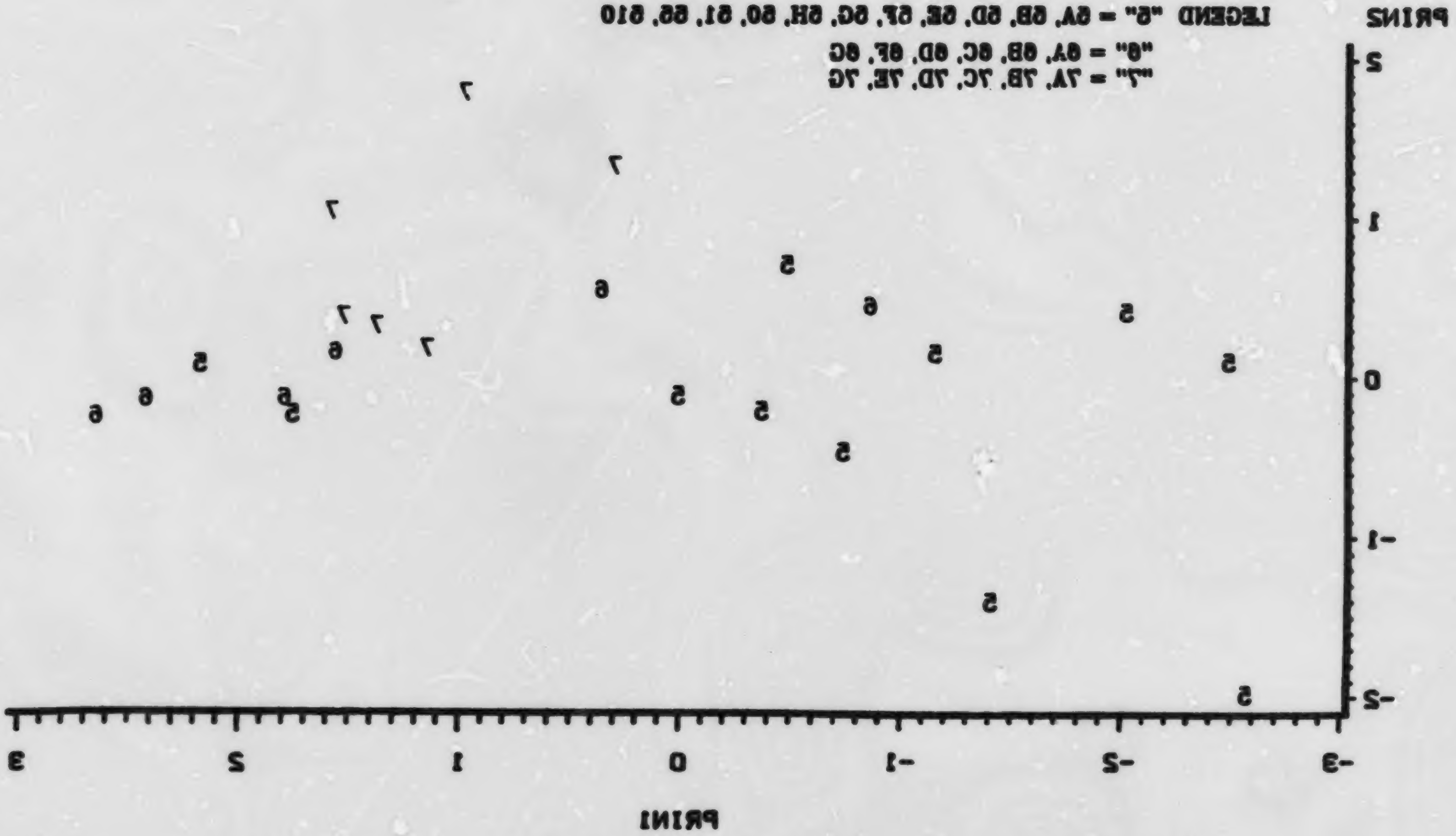

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FIGURE 8.3 SCORE PLOT OF THE TWO HIGHEST PRINCIPAL COMPONENTS FOR METALS IN YEAR-2 AND YEAR-3 FINE SEDIMENTS FROM ENDICOTT FIELD AND MARINE STATIONS WEST. EACH POINT CORRESPONDS TO ONE STATION.

0231

sediments were collected. Points enclosed in diamond and square symbols identify the peat and river stations, respectively. This plot seems to indicate that the East and West Harrison Bay stations are somewhat distinct from the other stations. A similar pattern is repeated among the marine stations alone. Figure 8.3 shows that the "6" and "7" stations are somewhat distinct from the "5" (central Study Area) stations. Figure 8.4 also shows that the "1","2", "3", and "4" (eastern Study Area) stations are separated from the "5" (central Study Area) stations. This distinction or separation is largely confined, however, to the first principal component (PC) axis. In fact, the PCA showed that 44 percent of the variation among these scores could be accounted for by the first PC and only an additional 16 percent by the second PC. In other words, 60 percent of the information describing patterns of variation among stations, for these selected analyte concentrations, is represented in a plot of the first two PCs.

The evidence for a separation between the PCA scores of some river station groups, as well as marine station groups, supports the initial conclusion that the Beaufort Sea can be viewed as a collection of different geographic regions.

Figure 8.5 is a loadings plot for the PCA of metals. It shows that most of the variability in the first PC is due to chromium (Cr), copper (Cu), lead (Pb), vanadium (V), and zinc (Zn), all of which appear to make similar contributions. Vanadium makes the largest relative contribution to explaining the observed variation among stations. The relative contribution of cadmium to the first PC is smaller and is very different from contributions of the other metals mentioned above, as indicated by the sign (negative) of its loading. Barium also makes a relatively small contribution to the first PC but makes the largest contribution of all metals to the second PC. It is also interesting to note that zinc makes a relatively large contribution to both PCs. It is evident from this loadings analysis that the pattern of variation in all metals, except barium and cadmium, is very similar. An interpretation of this pattern is that chromium, copper, lead, vanadium, and zinc behave as one metal.

Figure 8.6 is the score plot for the PCA of hydrocarbon concentrations. The patterns that emerge from this plot are similar to those for the metals, although river and peat stations appear to be more distinct from marine stations. River stations corresponding to the "6" (East Harrison Bay) stations are distinct from those corresponding to the "5" (central Study Area) stations. This distinction occurs primarily in the second PC.

The hydrocarbon PCA results indicate that 67 percent of the variation among stations is accounted for by the first PC. An additional 18 percent of unexplained variation among the

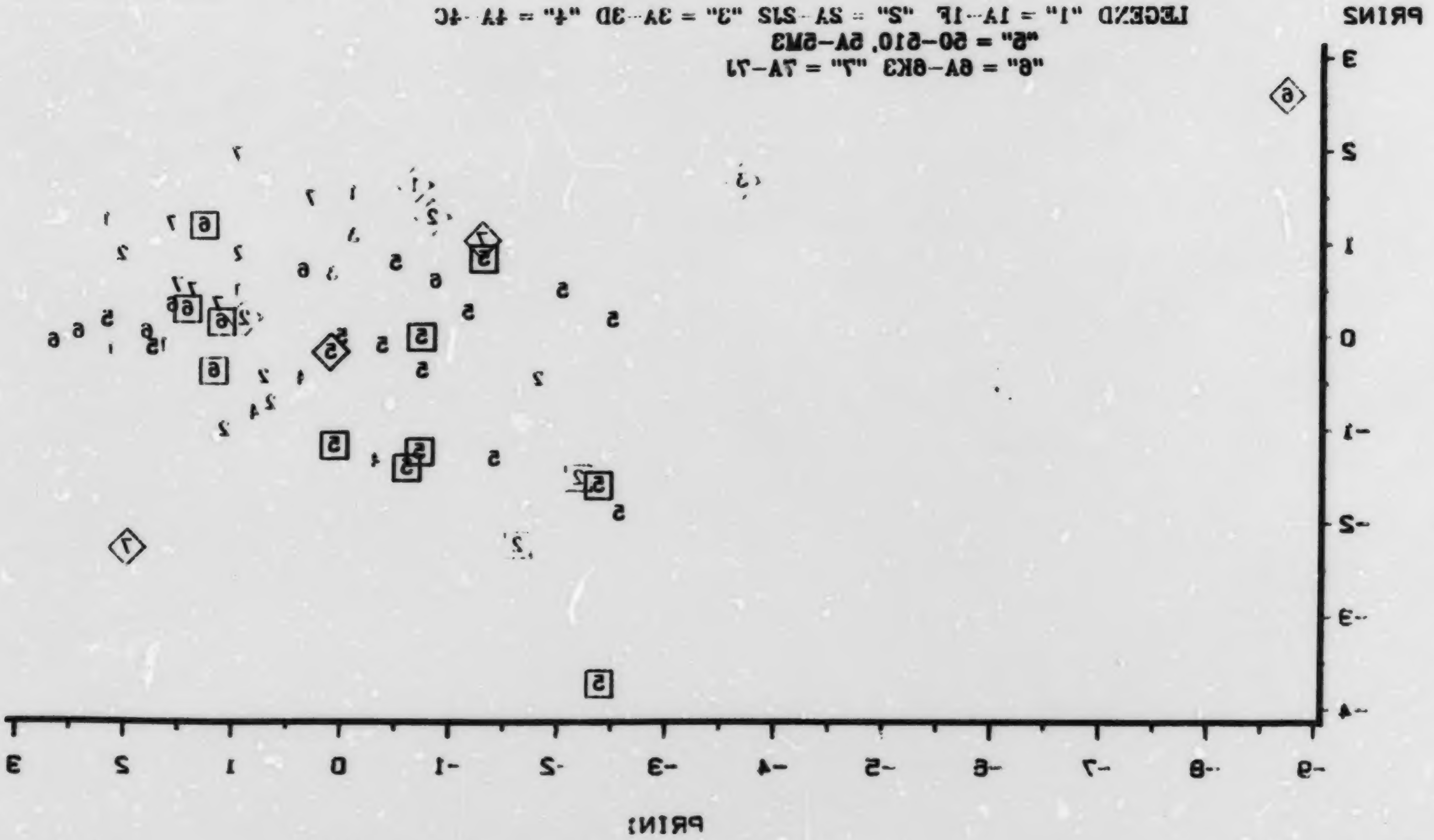

FIGURE 8.2 SCORE PLOT OF THE TWO HIGHEST PRINCIPAL COMPONENTS FOR METALS IN YEAR-2 AND YEAR-3 FINE SEDIMENTS. EACH POINT CORRESPONDS TO ONE STATION (DIAMOND-PEAT, SQUARE-RIVER).

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8.4 MULTIVARIATE PATTERN RECOGNITION IN SEDIMENT CHEMISTRY

A Principal Components Analysis (PCA; Sharaf et al., 1986; Johnson and Wichern, 1982) was performed using sediment chemistry data from each marine, peat and river station. The primary objective of this type of statistical analysis is pattern recognition. Patterns or trends among stations may not be clear by viewing the plots of just two analyte concentrations at a time, or by examining all the correlations between every pair of analytes. However, the use of PCA will show groupings of stations where variations in data are similar. A second objective of PCA is to determine the relative contribution of each analyte concentration toward the identified patterns or trends. A more detailed explanation of PCA is given in Appendix D.

Two separate PCA analyses were performed, one using the metals data and the second using the hydrocarbon data. The trace metal data used in this analyses were for the fine sediment fraction analyzed in Year-2 and Year-3. The hydrocarbon data were for the bulk sediment for all three years. In each analysis, all data (replicates) were averaged over years to produce a single observation for each station.

Use of too many variables (analytes) that are sums or combinations of other variables may obscure the assessment of the relative importance of each variable in the PCA. Therefore, it is generally recommended that each variable used in the PCA make a clearly defined (unique) contribution of information to the analysis. For example, data for both TALK (total alkanes) and LALK (lower molecular weight alkanes) were not included in the PCA of hydrocarbons because TALK includes LALK. Instead, HALK (high molecular weight alkanes) and LALK were included in this analysis. For the same reason, data termed ISO were not included with pristane and phytane since ISO includes these two analytes. A new variable (ISODIFF) was created that represents the contribution of isoprenoids 1380, 1470, and 1650, and did not contain any information on either pristane (1708) or phytane (1810). ISO and ISODIFF are related by the expression:

ISODIFF = ISO - [pristane + phytane].

Results of the PCA analyses present two significant observations:

- There are no dramatically clear patterns among the stations.
- There is some evidence that geographic regions exist with similar sediment characteristics.

Figure 8.2 is the score plot for the trace metal PCA. Each point on the plot represents a single station where marine

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geometric mean. The percent standard error is the standard error of the logarithms of the analyte concentrations which are back-transformed (antilogs) to the original scale.

In order to give a more formal definition of the geometric mean and percent standard error, it is necessary to introduce the concept of a concentration variable. In this case, let x_{ij} be the ith concentration measurement of the jth analyte for a given sediment sample. The geometric sample mean is

$$\bar{X}_{g_i} = \exp\left[\sum_{j=1}^{n} Ln(x_{ij}) \Big/ n\right]$$

and the percent standard error of the geometric sample mean is

$$SE_{g_i} = \exp\left[\sum_{j=1}^{n}\left(Ln(x_{ij}) - \sum_{j=1}^{n} Ln(x_{ij})\right)^2 \Big/ (n-1)n\right]$$

The percent standard error of the geometric mean is treated differently than the standard error of the arithmetic mean. In the latter case, some sense of the variability about the arithmetic mean is obtained by adding or subtracting the standard error. In the case of the geometric mean, a sense of the variability is obtained by multiplying or dividing the percent standard error into the geometric mean.

8.3.2 Normalization

Normalization is also a useful mathematical transformation. Typically, a variable of interest (e.g., phytane) is divided by another ancillary variable (e.g., TOC). This procedure accomplishes two purposes. First, it ensures that comparisons among variables of interest are made on a more meaningful or adjusted basis. Second, the variance of the result is sometimes less than the variance of the original variable of interest.

Statistical analyses of normalized analyte concentrations have greater sensitivity. That is, relatively small differences in normalized analyte concentrations between years may be declared as statistically significant, while larger differences in the original variables of interest may not. However, in the two previous years of this study, unsuccessful attempts were made to discover a single ancillary variable or combination of variables that were useful in normalization. It was decided that this issue would not be pursued in the third year and that non-normalized data would be used in the statistical analyses.

that the observed changes are geochemical in nature (e.g., a change in sediment grain size or TOC is associated with a change in a specific metal or hydrocarbon parameter), the corresponding concentration changes may not be considered to be indicative of a drilling source. If no corresponding geochemical changes are documented, and significant increases are observed in petroleum source ratios, then such changes may be directly or indirectly related to oil and gas development.

The principal statistical inference method used in this investigation is an analysis of variance (ANOVA). A Bonferroni multiple comparison method (Miller, 1981) was used in those instances where several pairs of geometric means were tested for significant differences. The basis for this method lies in the fact that the greater the number of statistical tests performed, the greater the likelihood that at least one will be found to be significant, due to chance. The Bonferroni method makes an adjustment for this fact.

All statistical analyses were performed using PROC MEANS and PROC GLM of the SAS (Statistical Analysis System) computer software available on an IBM 4381 computer. The graphics in this chapter of the report were produced using the SAS/GRAPH software and printed on the QMS 1200 laser-graphics printer or the Hewlett-Packard 7470 desktop pen-plotter.

8.3 DATA TRANSFORMATION AND NORMALIZATION

8.3.1 Transformations

Chemical concentration data are typically assumed to be lognormally distributed (Sharaf et al., 1986) and, therefore, require a mathematical transformation before a statistical analysis is performed. Lognormally distributed data generally consist of many values at low concentrations and only a few values at higher concentrations. This means that the distribution of such data on their original scale is often skewed. However, the logarithms of these data usually do appear normally distributed. The statistical tests used in this study depend on the assumption that the data are normally and, therefore, symmetrically distributed. To preserve this assumption, the data were transformed by taking the natural logarithm of each analyte concentration value. This transformation was also used prior to data analysis in the two previous years of the program.

Mean concentrations for all analytes, averaged across years or across stations, are reported as geometric means. Geometric means are obtained by averaging the logarithms and back-transforming to the original scale. The geometric or percent standard error (Snedecor and Cochran, 1967) can also be calculated and is a measure of dispersion or variation about the

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Both ANOVAs showed that there are statistically significant year and station effects ($p < 0.05$). The geometric means are presented in Table 8.2, as well as information indicating which pairs of geometric means are significantly different on the basis of the Bonferroni multiple comparison criteria. For example, the numbers 3, 1, 2 under the label Years and below the geometric means for TOT/TOC, indicate an ordering of these yearly means from largest to smallest. That is, the Year-3 mean was the largest and the Year-2 mean was the smallest. In addition, if no lines are indicated below them, all geometric means are significantly different from one another at the Bonferroni level of significance (approx. $p = 0.016$). Similarly, lines underneath the station identifiers in Table 8.2 indicate that all geometric station means connected by these lines are not significantly different according to the same Bonferroni criterion. Station means not connected by the same line are significantly different (approx. $p = 0.008$).

It should also be noted, however, that for both TOT/TOC and N/P, there is a significant interaction effect ($p = 0.004$ and $p = 0.0013$, respectively). This means that the ratio of one geometric station mean to another was not constant from one year to another. For some stations, the concentrations of TOT/TOC or N/P increases from year to year, but for other stations they do not. This can be seen in the plots of the geometric station means of TOT/TOC and N/P, although interaction is more pronounced among the other analyte ratios.

Again, based on these analyses, there is little or no evidence for clear and consistent trends or for the conclusion that oil exploration and development activity is contaminating the marine sediments in the Study Area.

8.7 ANALYSIS OF ANALYTE GRADIENTS IN SEDIMENTS

As a demonstration of one type of analysis of the data, one can examine hypotheses Ho1 and Ho2 for a series of stations from a suspected source similar to a large pollutant source. Such a gradient analysis was attempted using the Colville River regional stations (6B, 6C, and 6D).

In Section 8.5.1 it was noted that Station 6B had unusually high concentrations of hydrocarbons. One probable explanation is that the Colville River, which empties into the Beaufort Sea in the vicinity of Station 6B, is transporting hydrocarbons, originating upstream, to the Beaufort Sea sediments. If the river is the vector of transport for these hydrocarbons, a declining concentration gradient should be detectable along a linear distance from the river mouth.

we would not expect to see such a trend in analyte ratios among years.

Seven stations had complete information on all hydrocarbon variables in each of the three years. Six of these stations (2F, 3B, 4A, 5D, 6D, and 7A) were chosen for investigation, one from each of six different station groups. With the exception of Stations 3B and 4A, each station also represents a different geographic region.

Appendix C, Section 5 presents figures illustrating the change in the annual geometric mean concentration of eight analyte ratios (PAH/TOC, TOT/TOC, P/D, N/P, LALK/TALK, ISO/ALK, Pristane/Phytane, and FFPI). It is clear from these figures that if a year-to-year trend exists, it is not the same for each ratio and may depend on the station being examined. Of these ratios, only TOT/TOC and N/P show a trend of increasing concentration from Year-1 to Year-3.

On the basis of these figures, only the TOT/TOC and N/P ratios appear to be changing with time. Therefore, a two-way fixed-effects ANOVA was performed for TOT/TOC and N/P using the following two-way fixed-effects model (Milliken and Johnson, 1984):

$$Y_{ijk} = u + s_i + r_j + sr_{ij} + e_{ijk}$$

where: Y_{ijk} = the ratio response value for the kth replicate of the ith station for the jth year.

u = grand mean of all observations

s_i = station effect

r_j = year effect

sr_{ij} = station-by-year interaction

e_{ijk} = random error

Each subscripted term in the above equation is an additive effect that modifies the grand mean (u) of all observations. Specifically, this model states that every individual observation can be viewed as a grand mean plus an effect due to the station it came from, the year it was measured, the fact that year and station effects may interact, and a random source of variation due to the repeated measurement of a station. An interaction effect assumes that the difference between the average ratio response between stations may not be constant from one year to another.

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TABLE 8.1 DESCRIPTIVE STATISTICS FOR CHEMICAL CONCENTRATIONS IN SEDIMENT SAMPLES OVER ALL MARINE STATIONS

TYPE OF CONCENTRATION	TYPE OF SEDIMENT	# NONMISSING VALUES	GEOMETRIC MEAN	% STD ERR OF GEOM. MEAN	LOWER 95% CONF. LIMIT FOR G.M.	UPPER 95% CONF. LIMIT FOR G.M.
N	BULK	3	0.15	1.10	0.12	0.18
F	BULK	3	0.032	1.09	0.028	0.038
P	BULK	3	0.13	1.20	0.09	0.18
D	BULK	3	0.023	1.23	0.015	0.035
PAH	BULK	3	0.10	1.05	0.09	0.11
PHYT	BULK	3	0.023	1.09	0.019	0.027
PRIS	BULK	3	0.050	1.09	0.042	0.058
LALK	BULK	3	0.68	1.07	0.59	0.78
TALK	BULK	3	4.03	1.09	3.38	4.80
TOT	BULK	3	11.47	1.12	9.24	14.24
BA	FINE	2	334	1.05	306	364
CD	FINE	2	0.17	1.11	0.14	0.21
CR	FINE	2	83	1.11	68	101
CU	FINE	2	22.1	1.01	21.6	22.6
PB	FINE	2	12.3	1.11	10.1	15.0
V	FINE	2	114	1.02	110	119
ZN	FINE	2	91	1.00	90	92
TOC	BULK	3	7.60	1.10	6.32	9.13
MUD	BULK	3	27.9	1.08	24.2	32.2
FFPI	BULK	3	77	1.02	74	80
ISO/ALK	BULK	3	0.452	1.03	0.428	0.478
LALK/TAL	BULK	3	0.170	1.17	0.124	0.232
PRIS/PHY	BULK	3	2.1	1.08	1.9	2.5
N/P	BULK	3	1.2	1.10	1.0	1.4
P/D	BULK	3	5.6	1.10	4.7	6.8
PAH/TOC	BULK	3	0.013	1.08	0.011	0.015
TOT/TOC	BULK	3	1.5	1.18	1.1	2.1
BA/CR	FINE	2	4.0	1.16	3.0	5.4
BA/V	FINE	2	2.9	1.07	2.6	3.3

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Table 8.1 presents a summary of the geometric mean concentrations of all analytes in the Beaufort Sea for both the fine fractions and bulk marine sediments. Each geometric mean is an average over all stations and all years. An estimate of the percent standard error was obtained by computing the variance among the three yearly mean concentrations.

Also included in Table 8.1 are the upper and lower confidence limits for the geometric mean. The upper 95 percent confidence limit is calculated by multiplying the geometric sample mean by the quantity [exp(1.96SE)], where SE is the percent standard error. The lower 95 percent confidence limit is calculated by dividing the geometric sample mean by the same quantity. The resulting confidence interval for each analyte is a statement of probability. In other words, intervals defined by these upper and lower bounds will contain the true values of a geometric mean analyte concentration 95 percent of the time. All variables in Table 8.1 are measured in µg/g (ppm) with the exception of TOC, which is expressed in mg/g. All ratio variables are unitless except for PAH/TOC and TOT/TOC, which are measured in µg/mg.

The variables P (phenanthrenes) and D (dibenzothiophenes) appear to have the most variation among all stations and years as indicated by the two highest percent standard errors (1.20 and 1.23, respectively).

Such Study Area-wide considerations are of general interest if one considers the entire Study Area (i.e., the nearshore) or the Beaufort Sea as a whole.

8.6 ANALYSIS OF ANALYTE RATIOS IN SEDIMENTS

In order to address hypothesis Ho2, and ascertain whether the sediment data show any effects due to past or present oil-related activity, ratios of several analytes were formulated and were analyzed by statistical methods.

In these analyses, analyte ratios such as Ba/Cr or N/P were examined for trends indicative of drilling mud or oil inputs. If contamination is occurring, we would expect to see these ratios change, moving in the direction of ratio values for source materials (i.e., oil or drilling mud). Because the potential contamination is likely to be an accumulative process, analyte ratio concentrations would be changing from one year to another or, when a gradient from a particular suspected source is being analyzed, the ratio would approach the value for the source as the source was appoached. If, during the three-year study, there was minimal oil exploration activity in the Beaufort Sea, East Harrison Bay: 6A, 6B, 6C, 6D, 6F, 6G

West Harrison Bay: 7A, 7B, 7C, 7D, 7E, 7G

Appendix C, Section 3 contains tables presenting the geometric mean concentration, percent standard error, and the 95 percent confidence limits for each geographic region of the Study Area. These figures show the geometric mean concentrations of each analyte among all regions in the Study Area. One analyte is represented in each figure.

Hydrocarbon concentrations appear to be consistently higher in the East and West Harrison Bay regions. Hydrocarbon concentrations also appear to be consistently lower in the Camden Bay, Foggy Island Bay and Endicott Field regions than in other Study Area regions, and lowest in the Foggy Island Bay. This trend supports the idea that viewing the Beaufort Sea Study Area as a collection of geographic regions is a useful concept.

It is also interesting to note that the above pattern among regions is nearly identical to the patterns demonstrated for percent mud and TOC, although the TOC pattern is not as pronounced as with percent mud or among the hydrocarbon variables.

Sediment trace metal concentrations show an entirely different regional pattern than the hydrocarbons. These patterns are not as consistent as those for hydrocarbons and vary with different metals. But the patterns contribute more, albeit weaker, evidence in support of characterizing the Beaufort Sea Study Area by region.

Barium and chromium show similarities, with the highest concentrations evident in the West Harrison Bay region. Although the geometric means are fairly equivalent among all other regions for both analytes, there is more variability in barium among regions than in chromium. Copper and lead show similar patterns also. The highest concentrations of these metals occur in the Camden Bay and East Harrison Bay regions. Copper is also more widely variable than lead among regions. Vanadium and zinc show almost identical patterns in both geometric mean concentration and variability. Their scale of measurement is also similar. But cadmium is unique, exhibiting the highest concentrations in the Endicott Field region. Note, however, that cadmium concentrations are several orders of magnitude lower than those of most of the other metals.

8.5.3 Characterization of Analyte Concentrations in the Entire Study Area

Appendix C, Section 4 presents a tabular listing of all data (individual replicates and composites) for each station and year, and for both the bulk and fine fractions of the sediment samples where and when such analyses were performed.

presented for both the fine fractions and bulk sediments.

The figures in Appendix D, Section 2 illustrate the yearly geometric mean concentrations of each analyte of interest among all marine stations for both the fine fraction and the bulk sediment. These figures show the year-to-year variation for each station and are more useful for identifying trends or patterns among stations. These figures also illustrate one of the conclusions of the principal component analysis discussed in Section 8.4 (i.e., there are not many clear and consistent trends in these data).

Barium and cadmium concentrations, for example, appear to have opposite geographic trends. Barium concentrations are higher at the eastern and western stations (i.e., the "1" and "7" stations, respectively) in the Beaufort Sea than at the stations in between (i.e., the "2", "3", "4", "5", and "6" stations). Cadmium, on the other hand, is lower in concentration at these same eastern and western stations than at the stations in between. Chromium shows much higher concentrations among the western stations, while lead shows higher concentrations in the eastern stations. Vanadium and zinc show no clear geographic trends.

The geometric mean metal concentrations in bulk sediments across all marine stations are also included in Section 2 of Appendix C. Although there are no geographic trends in percent mud (silt + clay) among stations, total organic carbon (TOC) appears to be slightly higher and more variable in the western station groups. There does not appear to be any geographic trend among hydrocarbon concentrations, supporting the conclusion that there are few clear and consistent trends in the Study Area. However, Station 6B is consistently higher in hydrocarbon concentrations than any other station.

8.5.2 Characterization of Analyte Concentrations for Geographic Regions of the Beaufort Sea

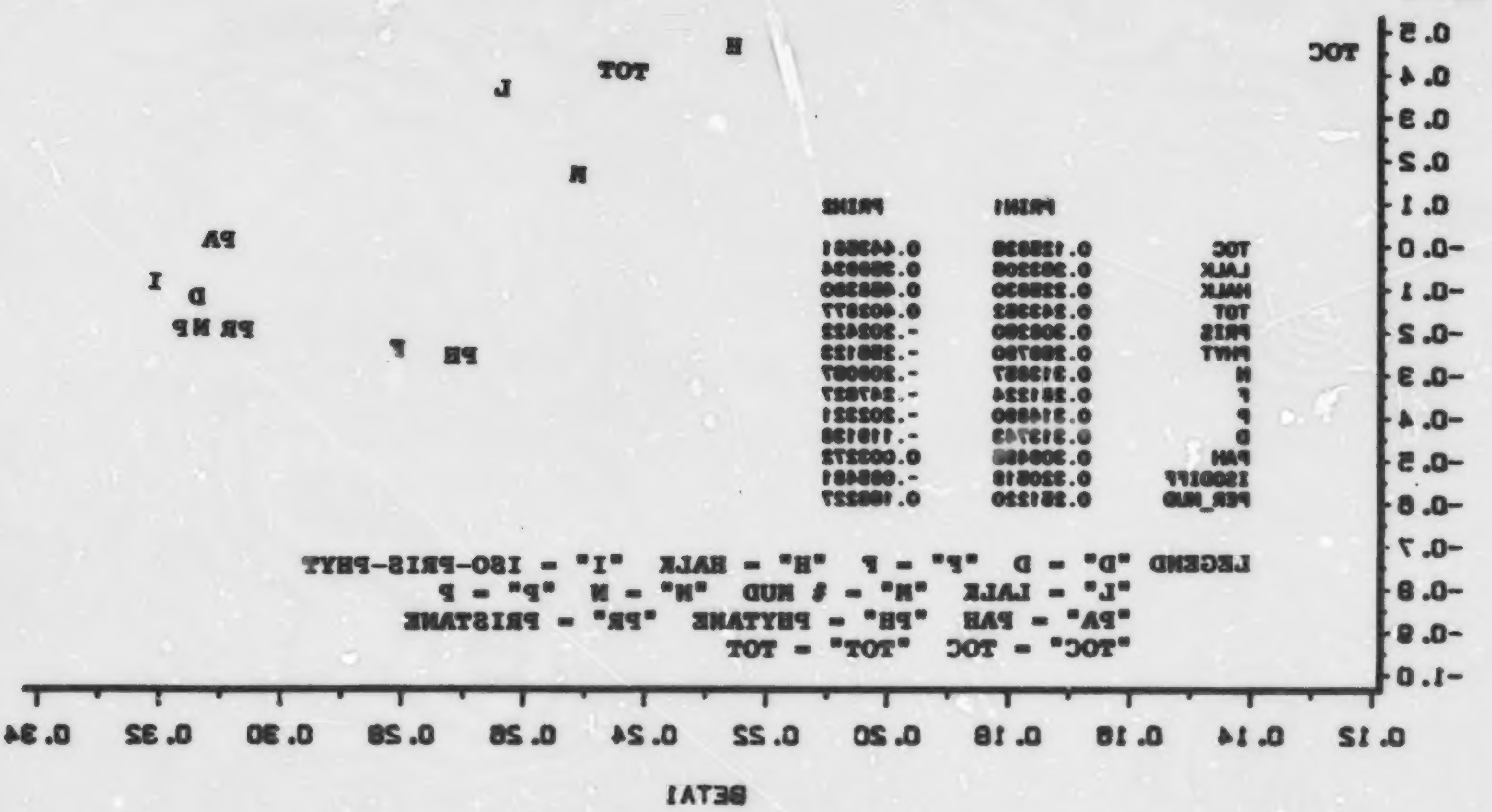
The Beaufort Sea Study Area was divided into six geographic regions. Each region was composed of stations from one or more similarily numbered station groups (see Figure 1.3). Each region was composed of the following stations:

Camden Bay: 1A, 1B, 1C, 1D, 1E, 2A, 2B, 2C, 2D, 2E, 2F

Foggy Island Bay: 3A, 3B, 4A, 4B, 4C, 5G, 5H

Kuparuk River: 5A, 5B, 5D, 5E, 5F

Endicott Field: 5(0), 5(1), 5(5), 5(10)



	PRIN1	PRIN2
TOC	0.128838	0.443881
LALK	0.283208	0.289934
HALK	0.228830	0.488380
TOT	0.243382	0.402877
PRIS	0.308280	-.302422
PHYT	0.288780	-.288123
M	0.313887	-.209087
F	0.281224	-.247827
P	0.314880	-.202321
D	0.313743	-.119138
PAH	0.3004[illegible]	0.003272
ISODIFF	0.320818	-.088481
PER_MUD	0.281220	0.108227

LEGEND "D" = D "F" = F "H" = HALK "I" = ISO-PRIS-PHYT
"L" = LALK "M" = % MUD "M" = M "P" = P
"PA" = PAH "PH" = PHYTANE "PR" = PRISTANE
"TOC" = TOC "TOT" = TOT

FIGURE 8.9 LOADINGS PLOT OF THE TWO HIGHEST PRINCIPAL COMPONENTS FOR HYDROCARBONS IN BULK SEDIMENTS FOR ALL YEARS. EACH POINT CORRESPONDS TO ONE CHEMICAL. LETTERS AT EACH POINT GIVE FIRST LETTER OF THE CHEMICAL NAME.

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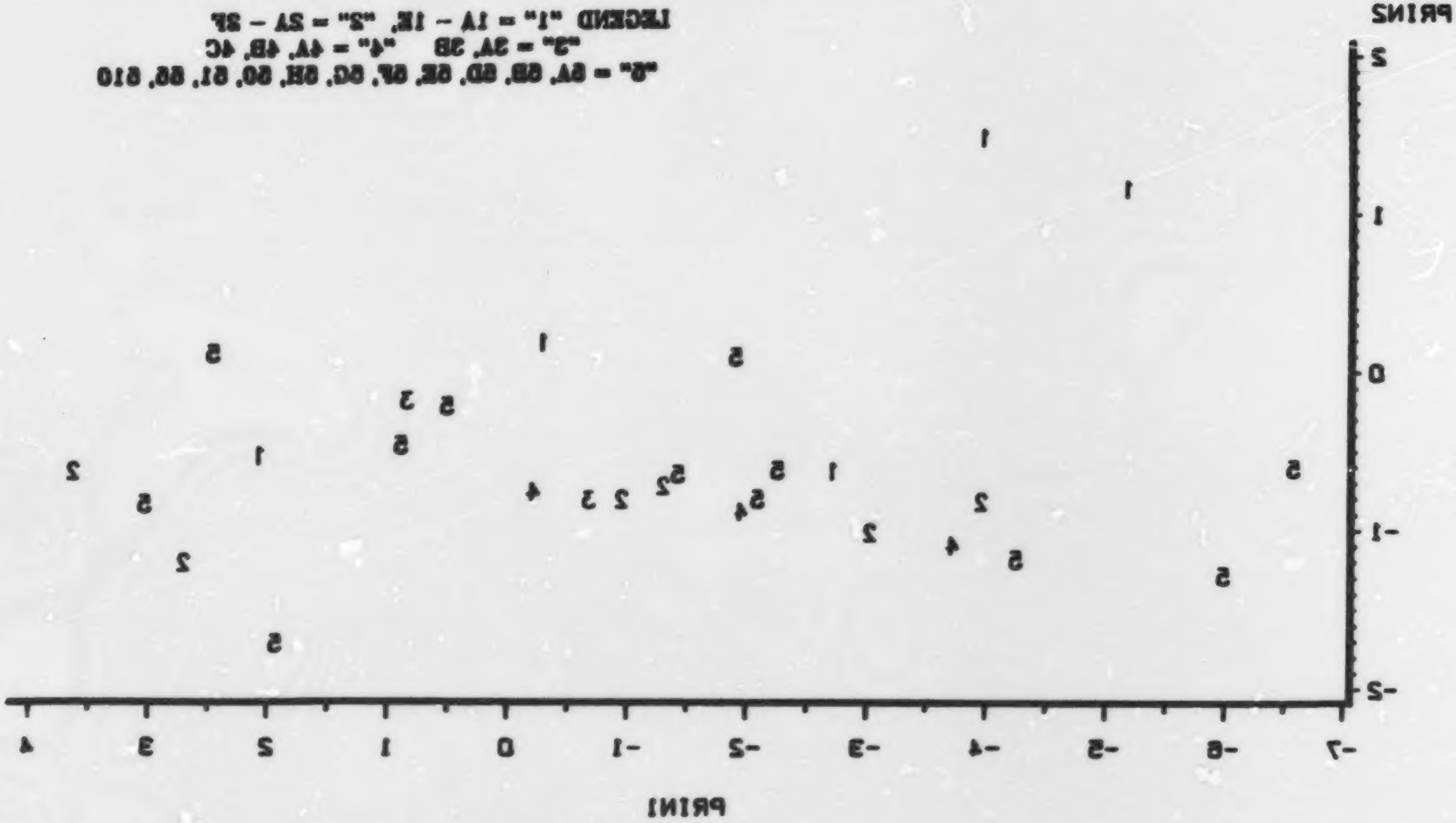

FIGURE 8.8 SCORE PLOT OF THE TWO HIGHEST PRINCIPAL COMPONENTS FOR HYDROCARBONS IN BULK SEDIMENTS (ALL YEARS) FROM ENDICOTT FIELD AND MARINE STATIONS EAST. EACH POINT CORRESPONDS TO ONE STATION.

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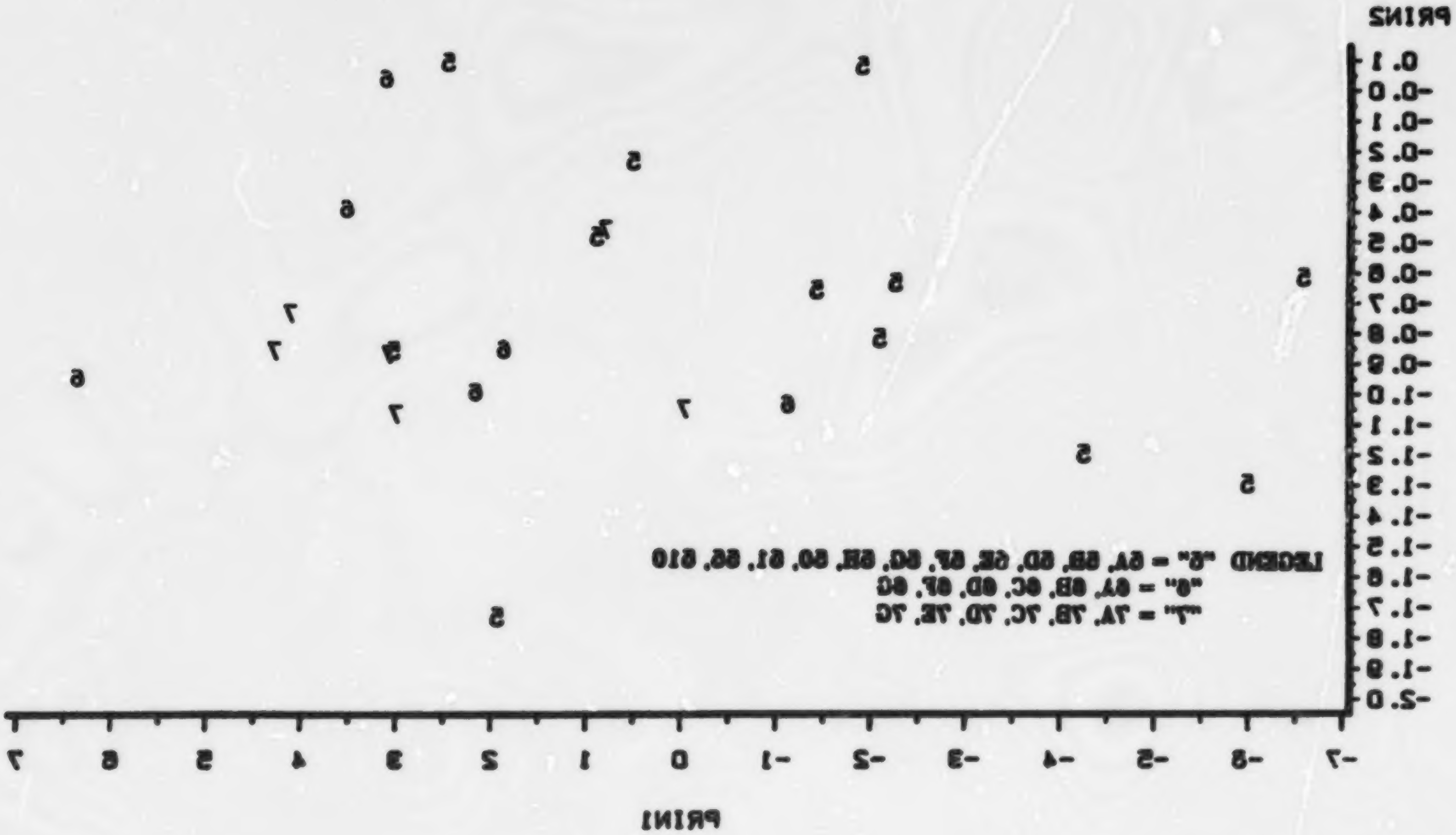

FIGURE 8.7 SCORE PLOT OF THE TWO HIGHEST PRINCIPAL COMPONENTS FOR HYDROCARBONS IN BULK SEDIMENTS (ALL YEARS) FROM ENDICOTT FIELD AND MARINE STATIONS WEST. EACH POINT CORRESPONDS TO ONE STATION.

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stations is accounted for by the second PC. That is, 85 percent of the information describing the patterns of variation in hydrocarbon concentrations among stations can be represented in a plot of the first two PCs.

Figure 8.7 shows that the "6" and "7" (Harrison Bay) stations are distinct from the "5" (central Study Area) stations. There is, however, more overlap among these station groups in the PCA of hydrocarbons than in the PCA of metals. Also, unlike the PCA for metals, this overlap is almost complete for station groups "1" through "5" and can be seen clearly in Figure 8.8.

Figure 8.9 is the loadings plot for the PCA of hydrocarbons. This plot shows that the most important contributors to the first PC are N (naphthalenes), P (phenanthrenes), D (dibenzothiophenes), pristane, PAH, and ISODIFF. As was noted with the trace metals, all of these hydrocarbon parameters appear to behave as one hydrocarbon variable. This plot also shows that TOC, TOT, LALK, and HALK make substantially larger contributions to the second PC relative to all other hydrocarbons. This latter finding is not as important as it would seem, however, since TOT, TOC, LALK and HALK only contribute 18 percent to the generalized variance (see Appendix D) not accounted for by the first PC.

Overall, the only significant pattern that emerges from the PC scores is a geographic one. Because little oil drilling activity occurred during the three-year study, the geographic pattern may be interpreted as a natural or inherent characteristic of the Beaufort Sea Study Area.

8.5 QUANTITATIVE SEDIMENT CHEMISTRY CHARACTERIZATION

The characterization of the concentrations of analytes in the sediments and determinations of the variability at each station, within each geographic region, or within the study area as a whole, is basic to determining if year-to-year or station-to-station changes are occurring. This is the basic premise of hypothesis Ho1. In this data set, which represents baseline conditions, it is important to fully define these baseline conditions to facilitate hypothesis testing when more intensive and more significant drilling does occur.

8.5.1 Characterization of Analyte Concentrations Among All Marine Stations

Appendix C, Section 2 contains tables presenting the geometric mean concentrations and confidence intervals for the same set of analytes, separately for each station identified during this study. These statistics were calculated directly from the data without the aid of an ANOVA model, and are

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of Station 6A to the Colville River. There was no significant difference between stations for any of the hydrocarbon parameters.

8.9 STATISTICAL METHODS FOR FUTURE ANALYSIS

As discussed previously (Section 8.1), an important component of this study is development of statistical analysis protocols for application to future monitoring efforts. When oil exploration and development activity increases in the future, an important environmental consideration will be demonstration of evidence for contamination effects due to such activity. Therefore, in the section that follows, hypothesis testing is presented with examples of statistical methods.

8.9.1 Aim of Future Analyses

The aim of future analyses will be to assess the change in selected analyte concentrations among stations and years by comparison to the baseline data obtained in this study. If such changes are detected, it will be desirable to determine whether chemical increases can be related to oil and gas exploration and development activities. The statistical analyses should address the four basic null hypotheses discussed in Section 1.0. Two of these hypotheses pertain to analyte concentrations in marine sediments and two pertain to analyte concentrations in the tissues of sentinel organisms:

Ho1: There will be no change in sediment concentrations of selected metals or hydrocarbons.

Ho2: Changes in concentrations of selected metals or hydrocarbons in sediments are not related to OCS oil and gas development activity.

Ho3: There will be no change in the concentrations of selected metals or hydrocarbons in selected sentinel organisms.

Ho4: Changes in concentrations of selected metals or hydrocarbons in selected sentinel organisms are not related to OCS oil and gas development activity.

Because hypotheses Ho1 and Ho3 are similar, they will be called type-Ho1 hypotheses. Likewise, hypotheses Ho2 and Ho4 are similar and will be referred to as type-Ho2 hypotheses.

TABLE 8.6 ANOVA RESULTS FOR ASTARTE (TWO-WAY MIXED-MODEL) AND CYRTODARIA (1-WAY RANDOM EFFECTS MODEL) TISSUE DATA TO DETECT YEAR-TO-YEAR VARIATION IN SELECTED PARAMETERS

	Astarte					Cyrtodaria			
	Yearly Geometric Means					Yearly Geometric Means			
Parameter	1	2	3	Year Effect (p-Value)[a]	Station Effect (p-Value)	1	2	3	Year Effect (p-Value)
N	0.0	0.005	0.002	0.003	0.056	0.0	0.003	0.014	0.001
F	0.0	0.002	0.0	NVC[b]	NVC	0.001	0.002	0.008	0.43
P	0.0	0.0035	0.002	0.005	0.24	0.002	0.0021	0.0038	0.09
D	0.0	0.0004	0.0	0.025	0.19	0.0	0.0	0.0014	0.004
PAH	0.0	0.0045	0.0048	0.65	0.65	0.0	0.0021	0.0022	0.004
Pris	0.0002	0.041	0.003	0.048	0.10	0.0	0.016	0.025	0.0001
LALK	1.12	1.03	0.06	0.0001	0.16	0.113	0.337	0.092	0.20
TALK	5.96	2.03	0.84	0.012	0.53	2.37	1.91	0.697	0.65
TOT	70.7	5.6	1.2	0.0001	0.63	30.2	9.6	6.1	0.11
Ba	20.0	26.0	20.0	0.0001	0.001	16.0	25.0	18.0	0.001
Cd	0.74	8.16	10.8	0.039	0.0001	0.47	1.48	1.54	0.11
Cr	2.29	3.01	2.96	0.68	0.006	2.12	2.83	2.67	0.045
Cu	21.0	21.0	17.0	0.001	0.0001	16.0	24.0	14.0	0.19
Pb	—	0.61	0.67	0.03	0.0001	—	0.50	0.72	0.0001
V	3.77	6.28	3.84	0.002	0.0001	3.26	6.41	4.81	0.003

[a] p-Values <0.05 can be considered statistically significant

[b] Not calculable

— No data collected during the year

Appendix C, Section 10 presents plots of each analyte concentration versus years for each combination of station and organism. For the metals, concentrations were highest for *Astarte* at Station 6D in every instance with the exception of zinc in Year-3. From the limited data set, there is no evidence for a detectable difference between *Astarte* and *Cyrtodaria* because both the lowest and highest metal concentrations were associated with *Astarte*. Barium, copper, and vanadium show a consistent increase in concentrations during Year-2. Because all three stations (Stations 3A, 5F, and 6D) are near river deltas, the increases may reflect greater river inputs of these metals to the Beaufort Sea during Year-2.

Overall, hydrocarbon concentrations in the tissues were very low. There are no apparent trends in the hydrocarbon data among the organisms from Stations 3A, 5F, or 6D.

The descriptive summaries and plots of the tissue data support the same conclusion reached with sediment data analysis (i.e., there is little evidence for contamination of sentinel organisms due to oil exploration). There is, however, notable variation in chemical concentrations from year to year. The latter conclusion that significant year-to-year variation exists can be tested statistically as described in the next section.

8.8.2 Statistical Analyses of Tissue Data

An ANOVA was performed on the *Cyrtodaria* data from Station 5F using a one-way random-effects model (Milliken and Johnson, 1984). The principal objective of this model was to determine if a significant year effect could be detected for each analyte concentration measured for this organism.

Table 8.6 illustrates the one-way ANOVA results. For two (Cd and Cu) of six metal parameters and five (F, P, LALK, TALK, and TOT) of nine hydrocarbon parameters, no significant year effect was detected. In other words, most of the metals showed significant variation among years, although this was true for less than half of the hydrocarbon analytes.

A two-way mixed-model ANOVA was used for the analysis of *Astarte* data from Stations 3A and 6D to determine if there was an effect due to years and/or a difference between stations. The results of the two-way ANOVA are also shown in Table 8.6. There is a significant ($p < 0.05$) year effect for all trace metals except chromium. Significant ($p < 0.05$) year effects were also detected for every hydrocarbon parameter except F (fluorenes). It is interesting to note that concentrations of all trace metals in *Astarte* were significantly ($p < 0.01$) higher at Station 6D than at Station 3A, probably due to the proximity

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TABLE 8.5 THREE-YEAR SUMMARY OF TISSUE ANALYSES

YEAR-1	YEAR-2	YEAR-3
Trace Metals Analysis		
3A Astarte	3A Astarte	3A Astarte
5F Cyrtodaria	5F Cyrtodaria	5F Cyrtodaria
6D Astarte	6D Astarte	6D Astarte
	1A Portlandia	
	1A+1B+1E Anonyx	
	1A+1B Astarte	
	2F Anonyx	
	3A Anonyx	
	4B Anonyx	
	5H Anonyx	
	5H Astarte	
	6D Macoma	
	6G Anonyx	
	6G Cyrtodaria	
	7B+7C Anonyx	
	7E Anonyx	
Hydrocarbon Analysis		
3A Astarte	3A Astarte	3A Astarte
5F Cyrtodaria	5F Cyrtodaria	5F Cyrtodaria
6D Astarte	6D Astarte	6D Astarte
6D Macoma	6D Macoma	
	1A Portlandia	1A Portlandia
	1A+1B Astarte	1A Astarte
		1B Astarte
	1A+1B+1E Anonyx	1A Anonyx
		1B Anonyx
		2F Anonyx
		5(1) Astarte
	4B Anonyx	
	5H Astarte	5H Astarte
		5H Anonyx
	6G Cyrtodaria	6G Cyrtodaria
	6G Anonyx	
	7B+7C Anonyx	7B Anonyx
		7C Anonyx
	7E Anonyx	7E Anonyx

8.8 TISSUE CHEMISTRY CHARACTERIZATION

An important component of this study included determination of trace metal and hydrocarbon concentrations in the tissues of sentinel marine organisms. Species were collected at various stations throughout the Study Area; due to limited availability of animals, and the time required to collect and process the samples, no attempt was made to sample every station. Species from some stations were pooled to form one sample in order to obtain enough biomass for analysis.

Table 8.5 summarizes the tissue sampling effort. Three genera (*Astarte*, *Cyrtodaria*, and *Macoma*) were collected from three stations in Year-1, and five genera (the three collected in Year-1, plus *Portlandia*, and *Anonyx*) were collected from 13 stations in Year-2 and 11 stations in Year-3.

8.8.1 Characterization of Analyte Concentrations Among Selected Animal Species

Appendix C, Section 8 contains a primary data listing for the tissue trace metal and hydrocarbon concentrations. Concentrations that were below detection limits are represented by a zero in the tables. A period (.) indicates either that no analysis was performed for the given year, station, and species or that such data did not exist.

Because some data values are specified as zeros, a more appropriate transformation of the data is $\log_e(10{,}000x + 1)$, where x is an individual analyte concentration. All statistical analyses were performed on transformed data and which were then back-transformed to the original scale for reporting purposes. Appendix C, Section 9 contains tables of geometric means and percent standard errors (including 95 percent confidence limits where applicable) for all analyte concentrations for which there were at least two years of data for each organism at a given station. These tables indicate that barium and copper concentrations were generally much higher than concentrations of other metals. However, only three stations had more than one year of trace metal data for any organism. The data also show that hydrocarbon concentrations were very low, regardless of the species or year collected.

Because there were only three stations (Stations 3A, 5F, and 6D) for which three years of data were available, the statistical analyses were confined to these stations. One organism (*Astarte*) was represented at both Stations 3A and 6D, while another organism (*Cyrtodaria*) was represented at Station 5F.

the ratio would stay the same along the concentration gradient), while non-natural inputs would not. For example, since barite is one of the principal constituents of drilling mud, we would expect to see, relative to other analytes, increasing concentrations of barium nearer a drilling rig. For example, a trend in the ratio of barium to chromium would be expected if oil exploration activity was contaminating the marine sediments with barite faster than for chromium. In the absence of drilling-related activity, it is expected that this ratio remain constant with distance from the source.

The figures in Appendix C, Section 7 attempt to show this relationship for the Colville River gradient. Only the data from Year-3 were used in these plots, which included a horizontal reference line for the geometric mean concentration of each analyte measured at three locations (Stations 6K1, 6K2 and 6K3) in the Colville River sediments. These figures illustrate the geometric mean of three replicate measurements of P and D for each station, the ratio of these two analytes; the means of LALK and TALK, and the LALK/TALK ratio; and the means of barium and chromium, and their ratio.

Two conclusions can b[illegible] drawn from these plots. Gradients in concentrations of all [illegible]ameters do exist. These differences are significant and, therefore, Ho1 is rejected for individual parameters. The second conclusion to be drawn from these plots, specifically the figures illustrating the P/D, LALK/TALK, and Ba/Cr ratios, is that the analyte ratios were not constant across the gradient. Given the overwhelming effect of the Colville River in determining metal and hydrocarbon concentrations in the area, constancy of analyte ratios was expected for this particular station transect. Unlike the data on individual analytes, the ratios did not show a clear trend. If the source in this case had been a drilling platform, a clear gradient in the ratio parameters, as well as in individual concentrations of analytes, would have been expected. This is because contaminated particles from the platform with ratios characteristic of drilling mud and/or oil would have mixed with particles having background ratio values (i.e., two end-members defining a mixing line or gradient), and this effect would be shown as linear mixing in the figures depicting the three analyte ratios.

Pursuant to this latter idea, a one-way ANOVA was performed on each of the three analyte ratios, modeling only for an effect due to stations. For both of the hydrocarbon analyte ratios N/P and LALK/TALK, no statistically significant station effect ($p > 0.10$) was determined. Although there was a significant station effect ($p = 0.0003$) for the Ba/Cr ratio, Station 6D did not fit the typical pattern of a concentration gradient (i.e., lower than values at Station 6C). Moreover, Station 6K had higher values than Station 6B, which may have contributed to the statistical significance of the observed station effect for the Ba/Cr ratio.

TABLE 8.4 MIXED-MODEL ANOVA RESULTS FOR THE DETECTION OF ANALYTE CONCENTRATION GRADIENTS IN SEDIMENT SAMPLES FROM THREE STATIONS IN THE BEAUFORT SEA

Parameter	Geometric Means by Station 6B	6C	6D	Station Effect (P-Value)	Comparison of Station Means[a] 6B vs 6C	6C vs 6D	6B vs 6D	Test Effect[b] (P-Value)	Interaction Effect[c] (P-Value)	Test for Decreased Linear Trend (P-Value)
N	1.67	0.32	0.12	0.019	*	*	*	0.54	0.086	<0.01
F	0.367	0.070	0.022	0.056	*	*	*	0.77	0.010	<0.025
P	0.72	0.26	0.09	0.020	*	*	*	0.35	0.030	<0.01
D	0.149	0.059	0.020	0.035	*	*	*	0.45	0.027	<0.025
EOM	0.53	0.19	0.07	0.035	*	*	*	0.36	—	0.0001
Phyt	0.098	0.032	0.017	0.0001	*		*	0.0003	—	0.0001
Pris	0.217	0.079	0.036	0.0001	*	*	*	0.0001	—	0.0001
LALK	2.19	1.00	0.67	0.0001	*		*	0.0001	—	0.0001
TALK	18.58	5.22	2.93	0.0001	*	*	*	0.0006	—	0.0001
TOT	47.8	24.1	8.14	0.0001	*	*	*	0.0007	—	0.0001
TOC	16.9	6.98	4.38	0.0001	*	*	*	0.085	—	0.0001
MUD	85.0	31.8	12.4	0.030	*	*	*	0.52	0.45	<0.025
Ba	496	312	333	0.015	*			0.53	—	0.018
Cd	0.23	0.14	0.11	0.0001	*		*	0.0015	—	0.0001
Cr	99	93	89	0.016			*	0.0001	—	0.0048
Cu	34.3	29.4	25.5	0.0002	*	*	*	0.23	—	0.0001
Pb	14.8	15.5	14.0	0.076				0.086	—	0.22
V	147	153	142	0.23				0.054	—	0.45
Zn	121	108	98	0.013			*	0.80	—	0.0038

[a] Using the Bonferroni Multiple Comparison Method (* = significant at the 0.05 level, otherwise blank)

[b] Using the method of Orthogonal Polynomials

[c] — indicates no interaction effect: data were reanalyzed with a model interaction term

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TABLE 8.3 GEOMETRIC MEANS FOR CHEMICAL PARAMETER CONCENTRATIONS FROM STATIONS 6B, 6C, AND 6D

TYPE OF CONCENTRATION	GEOMETRIC MEAN STATION 6B	GEOMETRIC MEAN STATION 6C	GEOMETRIC MEAN STATION 6D
N	1.87	0.22	0.12
F	0.387	0.079	0.022
P	0.72	0.38	0.08
D	0.149	0.080	0.020
PAH	0.53	0.19	0.07
PHYT	0.098	0.022	0.017
PRIS	0.217	0.073	0.038
LALK	2.19	1.00	0.87
TALK	18.58	5.22	2.93
TOT	47.80	24.11	3.14
TOC	19.89	8.99	4.38
MUD	88.0	31.8	12.4
BA	498	312	333
CD	0.23	0.14	0.11
CR	90	83	83
CU	34.3	20.4	28.3
PB	14.8	18.8	14.0
V	147	183	142
ZN	121	108	98

DATA FOR HYDROCARBONS AND AUX VARS ARE FROM BULK SEDIMENTS, YEARS 1,2,3

DATA FOR METALS ARE FROM FINE SEDIMENTS, YEARS 2,3

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Stations 6B, 6C and 6D were established along a linear transect extending from approximately 5 nmi from the mouth of the Colville River (6B) to about 15 nmi from that same reference point. The objective of this station transect analysis is to determine if, in fact, a gradient exists in analyte concentrations and whether this gradient is linked to the suspected source.

Table 8.3 displays the geometric mean analyte concentrations, averaged across years, for each of the three stations. This table shows that, with distance away from the river mouth (i.e., from Station 6B to 6D), there is a trend of decreasing concentrations for most variables. This trend is also much stronger and clearer for hydrocarbon variables than for the metals (see figures in Appendix C, Section 6). Concentrations of mud and TOC also decrease away from the suspected source. These figures illustrate the yearly geometric mean concentrations of each analyte for each station. Note that for Ba, Cr, Pb, and V the gradients are not as well defined as among the hydrocarbon parameters.

A two-way mixed-model ANOVA was performed similar to the one specified for the analysis of analyte ratios (see Section 8.6). The results of these analyses are given in Table 8.4. For every analyte, except for Pb and V, there was a significant station effect. Furthermore, statistical tests using the method of orthogonal polynomials (Milliken and Johnson, 1984) were all significant for a linearly decreasing trend (i.e., a decreasing concentration gradient exists). For most analytes, the probability of erroneously concluding that a gradient exists when in fact it does not, is less than 1 in 100 ($p < 0.01$).

For the hydrocarbons N, F, P, and D, a significant interaction effect ($p < 0.05$) was also found. This means that the year-to-year variation in these analyte concentrations was not constant from one station to another. This suggests that further investigations should focus on a gradient analysis within a single year. Most of the other analytes showed no interaction effects, but did show significant year effects (generally, $p < 0.01$). So, in addition to detecting a decreasing concentration gradient with increasing distance from the river mouth, these analyses also showed that there is a significantly large component of year-to-year variation in analyte concentration relative to the random variation that results from repeated measurements of these concentrations.

Once the concentration gradient has been confirmed and $H_{o}1$ falsified, we would like to know if the concentration gradient could be attributable to natural patterns of deposition or to anthropogenic inputs of suspected pollutants to marine sediments. This is the essence of Ho2. Natural inputs would accrue in the same relative proportions among analytes (i.e.,

TABLE 8.2 YEARLY GEOMETRIC MEANS FOR RATIO VARIABLES IN BULK SEDIMENTS

RATIO=N/P	STATION						
	2F	3B	4A	5D	6D	7A	ALL STATIONS
	GEOMEAN	GEOMEAN	GEOMEAN	GEOMEAN	GEOMEAN	GEOMEAN	GEOMEAN
YEAR							
1	0.4886	0.9188	0.8374	0.8370	0.8844	1.2840	0.8844
2	0.8088	0.8734	1.2034	1.3242	1.3773	2.0177	1.1270
3	0.7000	1.2285	0.9418	1.4787	1.8184	1.8471	1.2824
ALL YEARS	0.8879	0.8800	0.9869	1.1204	1.2841	1.8187	1.0271

YEAR 3 2 1

STATION 7A 6D 5D 4A 3B 2F

RATIO=TOT/TOC	STATION						
	2F	3B	4A	5D	6D	7A	ALL STATIONS
	GEOMEAN	GEOMEAN	GEOMEAN	GEOMEAN	GEOMEAN	GEOMEAN	GEOMEAN
YEAR							
1	1.9074	1.4812	1.7289	1.1831	2.0422	1.8708	1.8122
2	0.3828	1.8817	0.7181	1.8746	1.2222	2.1847	1.1818
3	1.7883	1.8880	1.8333	2.0888	2.8488	3.0482	2.0008
ALL YEARS	0.9948	1.8888	1.3481	1.8081	1.8024	2.3474	1.8308

YEAR 3 1 2

STATION 7A 6D 3B 5D 4A 2F

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8.9.2 Testing Ho1-Type Hypotheses

Time and cost considerations prohibited analysis of a sample size larger than three sediment grabs per station. It may, therefore, be desirable to determine the minimum detectable multiplicative changes in analyte concentrations for this sample size. Table 8.7 gives the minimum detectable percent change in an analyte concentration for a fixed value of the percent standard error. The maximum percent standard error for any analyte concentration at stations encountered in this study (see Appendix C) is generally less than 3.0. According to Table 8.7, this means that any increase (above baseline) in the geometric mean analyte concentration of 15 percent or more would likely be declared statistically significant at the 0.05 significance level.

In order to illustrate the statistical methods that would be useful in testing the type-Ho1 hypotheses in future monitoring investigations, the Endicott Field transect stations [i.e., 5(0), 5(1), 5(5) and 5(10)] were selected for analysis. The primary objectives of this hypothesis-testing effort are

1. To determine if there has been a significant increase in the concentration of selected analytes over time.

2. To determine if this increase is consistent and proportionate among all stations.

Again, because of the nature of analyte concentration data, a natural logarithmic transformation of the data is required. Thus, the methods described below are based on a statistical analysis of the logarithms of the selected analyte concentrations.

A two-way fixed-effects ANOVA model, as described in Section 8.6 should be used to accomplish both objectives. In this model, both station and year are declared fixed effects. This means that we are interested in making inferences about this particular set of stations and years, and not about the entire population of stations that could have been identified or about analyte concentrations for any randomly chosen year.

The first objective, stated above, is accomplished by testing for a significant year effect. The second objective is accomplished by testing for a significant interaction effect. If the latter is significant, it is important to determine the pattern of this interaction. This pattern can be examined by plotting the yearly means separately for each station and displaying them on the same graph. Some stations may show an increase over time while others may not. Whether the plots are produced before the statistical analyses are performed is probably not important. However, a complete understanding

TABLE 8.7 DETECTABLE MULTIPLICATIVE CHANGES IN CONCENTRATIONS AS A FUNCTION OF PERCENT CHANGE IN STANDARD ERROR

% Standard Error	Multiplicative Change in Concentration with a Future Sample Size of 3
1.105	1.35
1.22	1.7
1.40	2.1
1.49	2.7
1.65	3.45
1.82	4.4
2.01	5.6
2.23	7.2
2.46	9.2
2.72	11.8
3.32	19.5
4.06	32.55
4.95	54.35
6.05	91.15
7.39	153.35

cannot be obtained without both the interaction plots and the statistical analyses. One advantage of initially producing the interaction plots is that it can readily be determined which parameters show year-to-year increases.

Appendix C, Section 11 presents plots of key parameters illustrating the relationships among the Endicott stations and yearly means. It is of particular interest to note that if the sediment mud content is markedly different among years, it may influence the sediment trace metal concentrations. In this case, it may be useful to consider an Analysis of Covariance (Snedecor and Cochran, 1967; Milliken and Johnson, 1984) where percent mud is specified as the covariate. This same reasoning for determining whether to use TOC as a covariate should also be employed after examining the yearly means for TOC (Section 11, Appendix C).

From these plots, it is apparent that no consistent trend exists among the hydrocarbon parameters from one year to another. However, it does appear that N, F, P and D concentrations all increase from Year-2 to Year-3, with the exception of Station 5(10). An increase in barium, chromium, and vanadium concentrations between Year-2 and Year-3 is also apparent.

Table 8.8 contains the multiple comparison (Bonferroni) results from three exemplary analyses, one each for barium, chromium, and vanadium concentrations. Lines connecting the year and station mean identifiers indicate that there is no significant difference ($p > 0.05$) among them by the Bonferroni multiple comparison criteria. The lack of statistical significance for any model effect in barium (including the interaction effect) is due to the large amount of variation in the logarithms of this analyte. This explanation is also true for vanadium, although there is some evidence for differences among stations. Chromium, however, shows a significant ($p < 0.05$) difference between Year-2 and Year-3 as well as among stations. But the significant interaction effect ($p = 0.0003$) indicates that these differences between years are not constant from one station to another. Station 5(1), for example, shows no increase at all in the geometric mean chromium concentration between years and may, in fact, be primarily responsible for this interaction. The logical conclusion of these analyses is that the Ho1-type hypotheses could only be rejected for chromium.

8.9.3 Testing Ho2-Type Hypotheses

In order to test the Ho2-type hypotheses directly, some understanding of the proximity of each station to oil drilling activity is essential. This concept of station proximity should incorporate the knowledge of the prevailing wind and water currents and not just the distance to the nearest oil drilling area. Developing this concept, however, may be very difficult

TABLE 8.8 YEARLY GEOMETRIC MEANS FOR METAL VARIABLES IN FINE SEDIMENTS

BARIUM	STATION				
	S0	S1	S10	S5	ALL STATIONS
	GEOMEAN	GEOMEAN	GEOMEAN	GEOMEAN	GEOMEAN
YEAR					
2	210	224	275	380	265
3	276	279	394	334	321
ALL YEARS	241	245	329	356	290

YEAR STATION

3 2 S(5) S(10) S(1) S(0)

CHROMIUM	STATION				
	S0	S1	S10	S5	ALL STATIONS
	GEOMEAN	GEOMEAN	GEOMEAN	GEOMEAN	GEOMEAN
YEAR					
2	51	69	62	70	62
3	72	69	74	81	74
ALL YEARS	61	69	68	75	68

YEAR STATION

3 2 S(5) S(1) S(10) S(0)

VANADIUM	STATION				
	S0	S1	S10	S5	ALL STATIONS
	GEOMEAN	GEOMEAN	GEOMEAN	GEOMEAN	GEOMEAN
YEAR					
2	85	76	98	107	93
3	102	92	98	110	101
ALL YEARS	93	82	98	108	97

YEAR STATION

3 2 S(5) S(0) S(10) S(1)

in practice, due to the interspersal of oil drilling sites throughout the Beaufort Sea. One possible test would be to compare nearshore versus offshore analyte concentrations. But this would only be useful if all oil drilling occurs at some specified distance offshore and the potential contaminants are likely to remain there. This also assumes that the stations could be partitioned, by consensus, into nearshore and offshore grouping. Clearly, testing Ho2-type hypotheses is more a matter of comparing analyte concentrations among stations than among years.

An alternative to using all stations in a single analysis while retaining the concept of proximity is a gradient analysis. As demonstrated with the transect Stations 6B, 6C, and 6D in the Colville River area, a natural gradient of chemical concentrations, decreasing with distance away from the mouth of the river, was identified. Monitoring stations in the path of prevailing wind or water currents may also show a declining concentration gradient (for selected analytes) with distance from the source (i.e., an active drilling area).

It is important to verify that the observed gradient is due to anthropogenic inputs originating from the drilling region rather than natural influxes that have their source upstream in major rivers. This distinction can be verified by comparing the analyte ratio concentrations along a single gradient. If there are significantly higher Ba/Cr ratios, for example, at the stations nearer to the drilling region than at stations farther away, then the observed gradient is probably the result of oil and gas exploration activity (National Academy of Sciences, 1983).

Of all stations in the Beaufort Sea Study Area, the Endicott Field stations [5(0), 5(1), 5(5), and 5(10)] are most likely to exhibit direct impacts of oil and gas exploration or development activity. These stations were initially established as part of the "activity-specific" sampling rationale to represent a 1-, 5-, and 10-mile gradient transect downstream of the Endicott Field development [5(0)].

Appendix C, Section 12, presents figures illustrating 10 analyte ratios for the Endicott stations in Year-2 and Year-3. It is expected that chemical concentrations would be highest at Station 5(0) and successively lower at Stations 5(1), 5(5), and 5(10) if the field were actively being developed and that ratios determined at stations closest to the source would approximate the ratio of the source. Although the pristane/phytane ratio indicates a gradient pattern, this is only observed in Year-2 and may not be significant. The gradient pattern is not evident for all other analyte ratios.

The same two-way fixed-effects ANOVA used to analyze individual analyte concentrations is also appropriate for the

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analysis of analyte ratios. Although it is of interest to compare mean concentrations among stations, only three analyte ratios (LALK/TALK, ISO/ALK, and TOT/TOC) showed any significant ($p < 0.05$) differences among stations. There was no significant interaction between year and station effects.

One recommended addition to future statistical analyses for gradients is the use of orthogonal polynomials (Steele and Torrie, 1981; Milliken and Johnson, 1984). This method consists of a series of linear comparisons among the station means that would permit a determination of whether the decline in concentration along the gradient is linear or nonlinear. Because the analyses are performed on the logarithms of the analyte concentrations, a linear decline in the logarithms implies that the decline is exponential on the original scale.

8.10 SUMMARY AND INTERPRETATION

There is a substantial amount of year-to-year variation in trace metal concentrations, although this variation is much greater at some stations than at others. However, the year-to-year variation among hydrocarbon parameters is generally larger relative to the variation among the metals. This conclusion is demonstrated in Table 8.9.

A likely explanation for fluctuations in chemical inputs to the marine sediments is that their sources are inland and transported to the Beaufort Sea by the numerous large rivers. This is a significant implication of the three-year study. The results of the gradient analyses support this hypothesis.

Part of the future monitoring effort should focus on gradient analyses. With the appropriate knowledge of prevailing wind and water currents, transect stations with the potential for demonstrating gradients could be established. Proper selection of the stations would allow detection of linear or quadratic declines in the analyte concentrations on the log scale. Nonlinear declines would suggest that observed contamination is restricted to the immediate area of the source. Stations along the gradient should be far enough apart to make the interpretation of a nonlinear decline in concentration along the gradient meaningful, but not so far apart that detection of the gradient could be lost. The latter may occur if the farthest station from source A in the potential gradient is actually nearer to source B and, therefore, affected by it. Gradients in key analyte concentrations can be interpreted by a consideration of the proximity to a suspected source and of key diagnostic ratios for the analyte parameters.

The Principal Components Analyses performed on these data give evidence that some groups of stations are different from other groups. If past oil exploration activity were an

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TABLE 8.9 RELATIVE VARIATION[a] AMONG ANNUAL GEOMETRIC MEAN CONCENTRATIONS OF SELECTED HYDROCARBONS AND METALS CALCULATED BY AVERAGING ACROSS ALL STATIONS

Variables	Relative Variation
N	0.40
F	0.22
P	0.69
D	0.83
PAH	0.20
Phytane	0.35
Pristane	0.32
LALK	0.28
TALK	0.35
TOT	0.44
Ba	0.17
Cd	0.41
Cr	0.39
Cu	0.05
Pb	0.40
V	0.08
Zn	0.02
TOC	0.37
MUD	0.29

[a] Relative Variation = (UCL - LCL)/ X_g

where: UCL = upper 95% confidence limit on the geometric mean

LCL = lower 95% confidence limit on the geometric mean

X_g = geometric mean

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important factor in characterizing the analyte concentrations at nearby stations, we would expect to see more distinct clusters of the corresponding PC scores in the score plots. It was also expected that such score clusters would be composed of stations from several station groups, because exploratory drilling has occurred in the past at several locations. With the three-year baseline data collected during the BSMP, this pattern was not observed, but may appear when drilling activity increases. The fact that some regional separation among the "5", "6", and "7" stations was shown by the analyses lends support to the concept of viewing the Beaufort Sea Study Area in terms of distinct regions. A regional concept may be useful, but the PCAs suggest that no more than three or possibly four regions are distinct. The univariate analyses (Appendix C, Section 3) suggest that the Endicott Field Stations are also a separate and distinct region of the Study Area, but the multivariate analyses (PCAs) did not distinguish the Endicott stations from other "5" (central Study Area) stations.

The separation between the river stations corresponding to the "5" and "6" (Harrison Bay) stations suggests a relationship between these particular river and marine stations. The obvious implication is that rivers contribute more chemical contaminants at some station groups or regions than at others. This evidence is corroborated by the results of the gradient analyses.

Variability in the three-year means representing baseline conditions has been established for each parameter at each station. The magnitude of the determined variabilities can be used in conjunction with results in Table 8.7 to determine the detectable change in the parameters of interest.

Finally, it has been shown that all four null hypotheses, established at the initiation of this monitoring program, can be addressed by the method of two-way Analysis of Variance (ANOVA). This statistical technique, combined with the method of linear comparisons among geometric means, permits detection of increases in chemical concentrations in sediments and tissues between years, and allows testing of the H_o2 type hypotheses that such increases are due to oil and gas exploration activity. It should also be emphasized that descriptive data analysis techniques, tables of means and plots of the data, have played an important role in understanding and characterizing the concentrations of chemical contaminants in the Beaufort Sea sediments and tissues.

9.0 PROGRAM SUMMARY

The three-year Beaufort Sea Monitoring Program was successful in accomplishing a broad range of goals defined at the initiation of the study. The required technical goals were completed successfully. In addition, the program was refined each year and resulted in the evolution of a successful monitoring design.

Recommendations for monitoring environmental impacts of oil and gas related activities, should monitoring be required in the U.S. Beaufort Sea, can be made on the basis of the overall success of the BSMP. The success of the program can be described in terms of four major components:

1. **Design of the Sampling Program**

   - The sampling design (station placement) was based on a mixed-sampling strategy, combining area-wide, area-specific, and gradient-specific approaches. This rationale resulted in a sampling program designed to be flexible enough to accommodate changes as necessary, and to allow detection of temporal and incremental changes in trace metal and hydrocarbon concentrations of the Beaufort Sea OCS. The three-year chemical data set suggested that reoccupation of the specific 39 stations is not critical for implementation of a monitoring program in the Study Area. Instead, one key aspect of a future monitoring program will be to base monitoring design on the concept of geographic regions delineated by similar geochemical behavior.

   - The sediment replication strategy, developed after the first year of the program, was feasible and provided the required analytical replication for statistical analyses. The oversampling strategy, designed to provide samples for archival and possible future analyses, was employed without placing an additional burden on the basic field sampling program.

   - Collection of animal samples for tissue analyses was conducted on an area-wide basis. The sampling design developed in the second year of the program resulted in samples of opportunity with emphasis on the selection of diverse feeding types. As with the sediment

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sampling design, the opportunistic oversampling strategy resulted in samples for archival and possible reanalysis without placing a burden on the field program.

2. Implementation of the Field Program

- The execution of the field program proved to be effective in completing the assigned tasks in an efficient manner.
- The vessel and field-sampling equipment selected for this program proved to be well suited for sampling in shallow nearshore Arctic waters.
- The modified Van-Veen grab consistently provided undisturbed surface sediment samples.
- Use of the Van-Veen grab to collect infaunal bivalve samples proved useful, but tedious in actual field use.
- The samples collected under this program proved to be uncontaminated by the procedures employed.

3. Analytical Methods

- The analytical methods employed in the three-year program provided precise, quantitative trace metal and hydrocarbon data.
- ZGFAA, ICAP, and XRF proved to be successful analytical techniques to establish background levels of the trace metals Ba, Cd, Cr, Cu, V, Zn, Pb in the Beaufort Sea Study Area.
- Reorientation of the trace metals program to analysis of the mud fraction of sediment samples, accomplished during Year 2, more precisely defined the background trace metal geochemistry.
- Analysis for saturated hydrocarbons by GC/FID and for aromatic hydrocarbons by GC/MS provided sufficient analytical sensitivity to document incremental changes in concentrations in sediment and tissue samples.

4. Statistical Analyses and Data Interpretation

- Due to the variability of the analytical results, statistical manipulation of the data is required to clearly present data trends. Interpretation of the data combined statistical and descriptive processes for data synthesis.

- Combined use of parameter ratios with the individual parameter concentrations provided the most useful approach to examination of the concept of source materials. Key diagnostic hydrocarbon ratios, particularly LALK/TALK and P/D, were shown to be important interpretive tools for detecting OCS-related petrogenic inputs to the Beaufort Sea, even though background levels are elevated.

- Hypothesis testing, a useful mechanism to assess the impacts of oil and gas development in the Study Area, could not be verified during the course of the study because of the low level of oil and gas development at the time of the study. Hypothesis testing was demonstrated through the river gradient analysis. This demonstration proved that hypothesis testing can be of use in a monitoring program.

- The results of the statistical analyses have produced concepts that can be relied upon in any subsequent monitoring program.

The three-year BSMP has resulted in a data set that defines the "present geochemical characteristics of the nearshore Beaufort Sea. Based on the success of this three-year program, the framework for future monitoring programs in the Beaufort Sea has been established.

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